Chapter 1: The Basics: Bonding and Molecular Structure

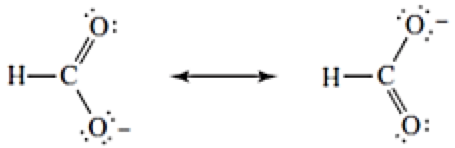
Practice Problems

1.1 ^{14}N, 7 protons and 7 neutrons; ^{15}N, 7 protons and 8 neutrons

1.2 (a) one (b) seven (c) four (d) three (e) eight (f) five

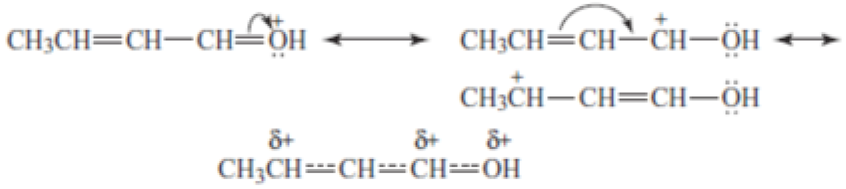
1.3 (a) ionic (b) ionic (c) covalent (d) covalent

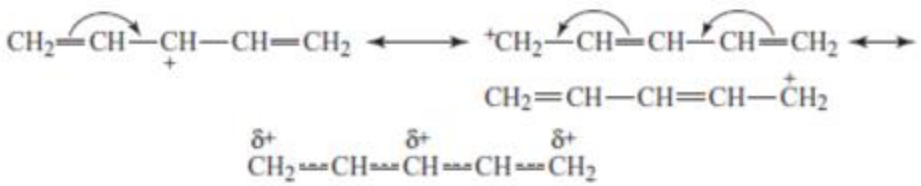
1.4

(a) 

(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

1.5

(a) 

(b) 

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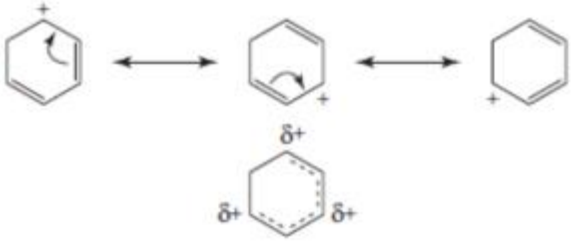
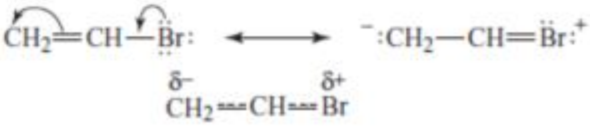
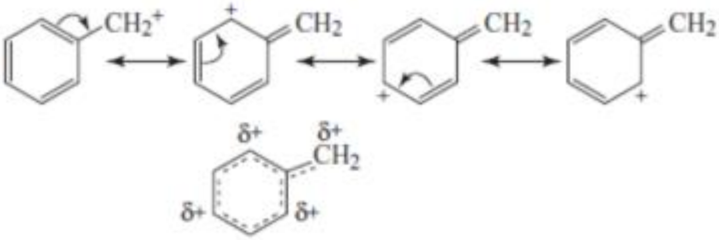
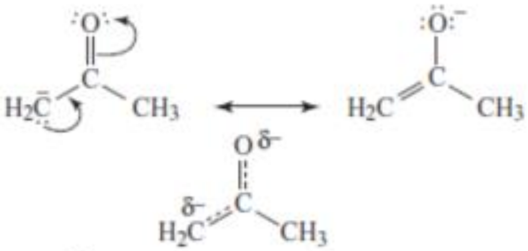
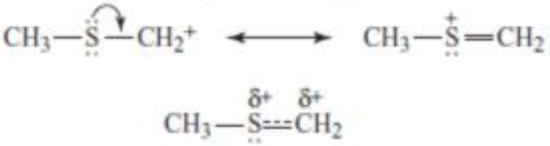
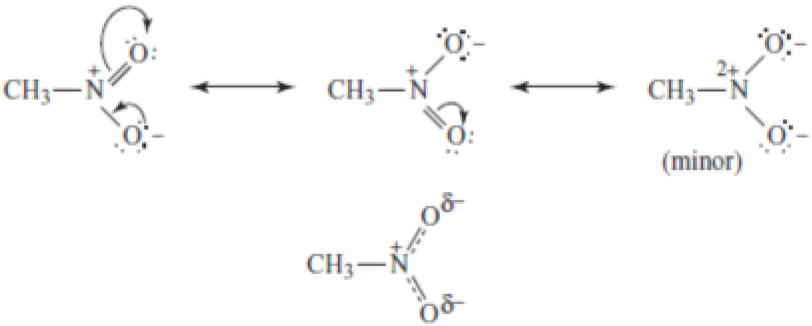
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

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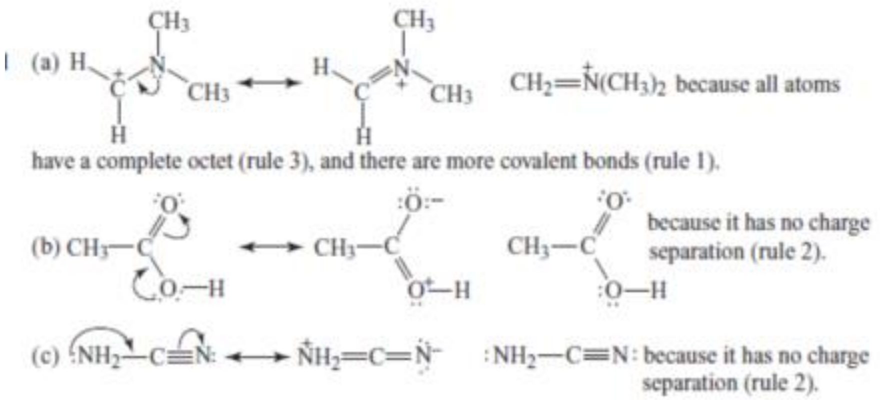
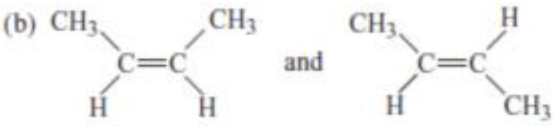
1.6

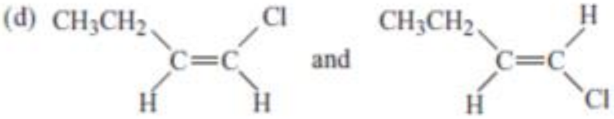


1.7

(a) Cis-trans isomers are not possible.



(c) Cis-trans isomers are not possible.



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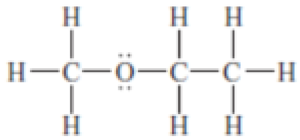
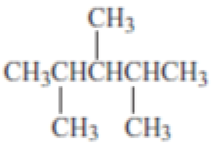
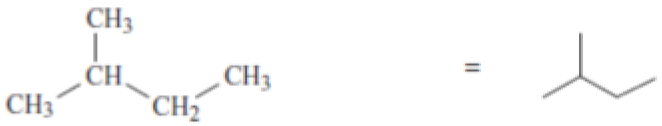


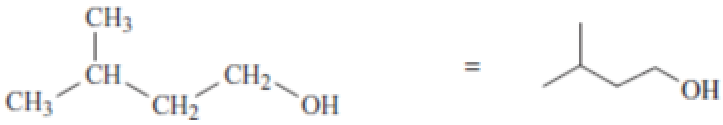


or $(CH_3)_2CHCH(CH_3)CH(CH_3)_2$

1.9

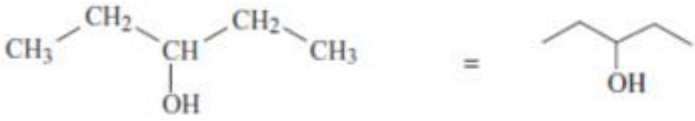
1.10

(a) 

(b) 

(c)

(d)

(e) 

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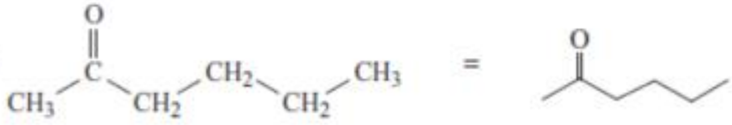
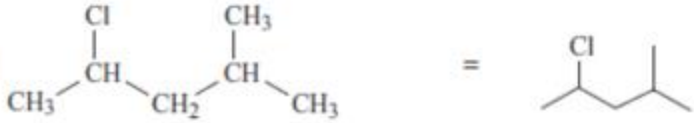
(g) 

(h) 

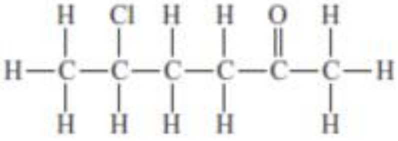
1.11

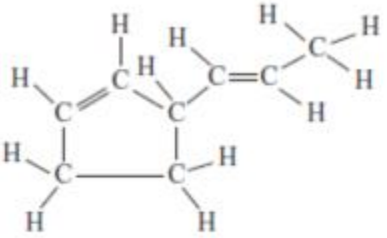
(a) and (d) are constitutional isomers with the molecular formula C_5H_{12}.

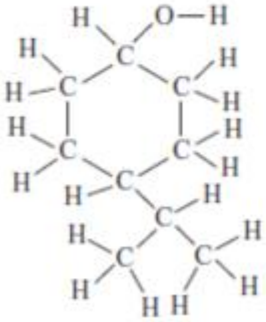
(b) and (e) are constitutional isomers with the molecular formula $C_5H_{12}O$.

(c) and (f) are constitutional isomers with the molecular formula C_6H_{12}.

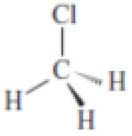
1.12

(a) 

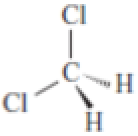
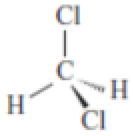
(c) 

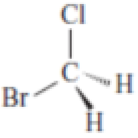
(b) 

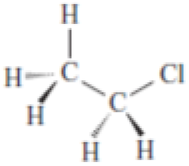
1.13

(a) 

(Note that the **Cl** atom and the three **H** atoms may be written at any of the four positions.)

(b)  or  and so on

(c)  and others

(d)  and others

Review Problems

1.14

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(a) Na^+ has the electronic configuration, $1s^22s^22p^6$, of Ne.

(b) Cl^- has the electronic configuration, $1s^22s^22p^63s^23p^6$, of Ar.

(c) F^+ and (h) Br^+ do not have the electronic configuration of a noble gas.

(d) H^- has the electronic configuration, $1s^2$, of He.

(e) Ca^{2+} has the electronic configuration, $1s^22s^22p^63s^23p^6$, of Ar.

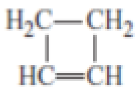
(f) S^{2-} has the electronic configuration, $1s^22s^22p^63s^23p^6$, of Ar.

(g) O^{2-} has the electronic configuration, $1s^22s^22p^6$, of Ne.

1.15

(a) $(CH_3)_2CHCH_2OH$

(b) $(CH_3)_2CH\overset{O}{\overset{\|}{C}}CH(CH_3)_2$

(c) 

(d) $(CH_3)_2CHCH_2CH_2OH$

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1.16

(a) $C_4H_{10}O$

(b) $C_7H_{14}O$

(c) C_4H_6

(d) $C_5H_{12}O$

1.17

(a) Different compounds, not isomeric

(b) Same compound

(c) Same compound

(d) Same compound

(e) Same compound

(f) Constitutional isomers

(g) Different compounds, not isomeric

(h) Same compound

1.18

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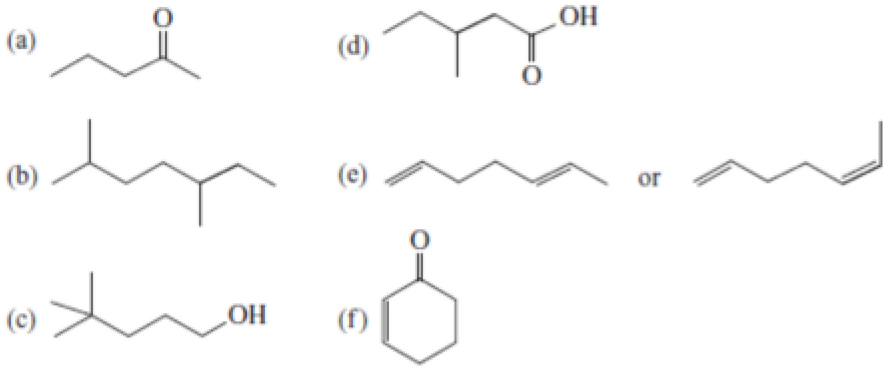
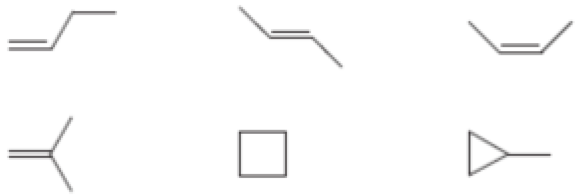


1.21



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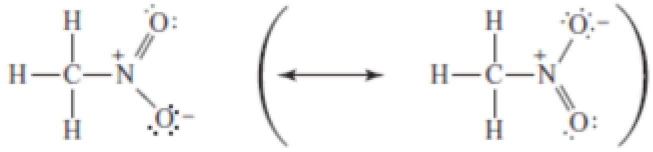
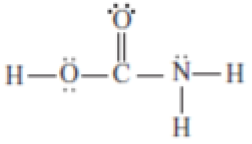
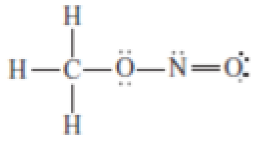
1.22







(Other structures are possible.)

1.23

(a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus *they are not resonance structures*. (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)

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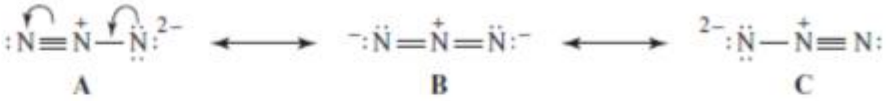
1.24

(a) and (b)

(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.

(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.

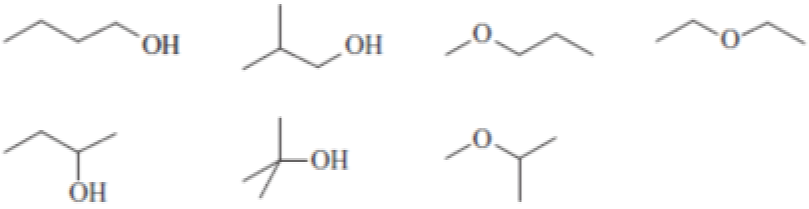
1.25



Structures **A** and **C** are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

1.27

(a)



(b) $(CH_3)_2NH$ $CH_3CH_2NH_2$

(c) $(CH_3)_3N$ $CH_3CH_2NHCH_3$ $CH_3CH_2CH_2NH_2$ CH_3CHCH_3 (with NH_2 on the central C)

(d)

<H1> **ADDITIONAL OBJECTIVE QUESTIONS**

<H2> **Single Correct Choice Type**

1. (c) It is a germinal halide as both the I are attached to the same C atom.

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2. **(b)** As extent of H bond is: carboxylic acid>alcohol.

3. **(a)** 2° carbons are C atoms attached directly to two other C atoms.

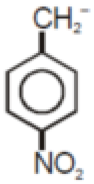
4. **(c)** II is not an acceptable structure as N can only accommodate a maximum of 8 electrons in the cationic state.

5. (b) DBE=4 ; No. of C (C) = 10.

DBE = (C+1) – (H)/2. Solving the equation for H, we get, H = 14

6. (b) $HC{\equiv}C{-}CH{=}CH_2$. The molecule has 3 pi bonds and 7 singma bonds (3 between C-C and 4 between C-H).

7. The question numbering is repeated and also the **question is WRONG!! No option is correct.**

8. (c) 

is most stable due to resonance of anion and the electron withdrawing effect of nitro group.

9. **(d)** I and III are more stable than II and IV due to resonance stabilization of the cation with the lone pair of O and formation of octet complete carbocation. I is more stable than III due to higher degree of carbocation. Similarly, II is more stable than IV due to higher degree of carbocation.

10. **(d)** Here the molecules shown are geometrical isomers about the left pi bond.

11. (d) An additional atom is present (H on N) which is not allowed in resonance structures.

12. **(c)** I and IV are not resonance structures as the H atom is moved and moving of atoms is not allowed in resonance.

13. **(c)** I and II are more stable resonating structures as they have an additional pi bond as compared to III and IV. II is more stable than I as it has the negative charge on N as compared to C. III is more stable than IV due to the negative charge on N as compared to C.

14. **(d)** It has an additional covalent pi bond in addition to complete octet of all the atoms.

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15. **(b)** Tertiary butyl carbocation [$(CH_3)_3C^+$] is the most stable of the given carbocations due to the maximum number of hyperconjugable alpha H atoms.

16.

16. **(b)** As the delocalization is only between the two pi bonds on the right, the pi bond on left is not in conjugation.

17. **(d)** It is resonance stabilized and it also has the highest degree.

18. (a) I, II and IV are the most stable free radicals as they are resonance stabilized and the stability order amongst them is based on the number of resonating structures. Amongst III,V and VI, higher the degree of free radical, greater is its stability.

19. **(d)** The *sp* C has two pi bonds while the sp^3 C has no pi bonds.

20. (d) The first carbocation is more stable due to resonance.

21. (a) In carbocation, hyperconjugation is between σ and empty p orbital of carbocation. While in alkene, hyperconjugation is between σ and π* orbital of the alkene.

22. (d) I is most stable due to two equivalent RS while II is also resonance stabilized anion. IV is more stable than III due to lesser extent of destabilizing +I effect of alkyl upon anion.

23. **(b)** z has the highest bond length of the three as it has purely single bond character. Y has more single bond character than x due to higher stability and contribution of the neutral RS as compared to the charged RS.

<H2> Multiple Correct Choice Type

1. (b), (d) In b, H atom is moved while moving of atoms is not allowed in resonance. In d, the second molecule has an extra atom (C atom), while atoms cannot be added or subtracted in resonance.

2. (a), (d) In resonance structures, only electrons are allowed to be moved and not atoms as in II where H atom is moved. Also the number of paired and unpaired electrons must remain same, which is not the case in III.

<H2> Linked-Comprehension Type

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1. (b) I, II and IV are resonance stabilized carbocations due to resonance between the carbocation and lone pair of N. The stability order amongst them is on the basis of degree of carbocation, higher the degree, higher the stability of carbocation. III is least stable as there is no resonance stabilization in it.

2. (a) I and II are more stable than III and IV due to one extra covalent pi bond in them. I is more stable than II as I is a neutral RS. III is more stable than IV as in III, negative charge is on more electronegative O atom.

3. (b) It will not show resonance as the pi bonds are not in conjugation.

4. (d) The carbocation and pi bond must be at alternate position for them to be in conjugation.

5. (c) There is resonance amongst the pi bonds present between C1-C2 and C3-C4, thus these bonds will have a character between a single and a double bond. While C6-C7 have a pure double bond between them, which is not in resonance, thus it has a lower bond length than C3-C4.

<H2> **Integer Type**

1. (4) The positive charge is delocalized on 4 carbon atoms due to resonance.

2. (6) Consider the benzene ring as a system and then see the hydrogen atoms present at adjacent (alpha) position to it. There is one H atom each on each of the six alpha C atoms.

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<H2> **Matrix Match Type**

1. (a)→(p), (q); (b)→(p); (r); (c)→(s); (d)→(s)

(a)→(p), (q) Resonance is between the lone pair and pi bond. Numbering for IUPAC name starts from the C atom attached to alcohol functional group.

(b)→(p), (r) Resonance is between the lone pair and pi bond. Numbering for IUPAC name starts from the C atom attached to alcohol functional group.

(c)→(s) No resonance as no conjugation. IUPAC name is 4-chlorocyclobutenol.

(d)→(s) No resonance as no conjugation. IUPAC name is 1-chlorocyclobut-2-enol.

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Chapter 2: Families of Carbon Compounds: Functional Groups and Intermolecular Forces

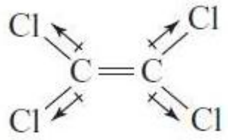
Practice Problems

2.1

The four carbon atoms occupy different positions in the two representations (cf. rule 2, Sec. 1.8A).

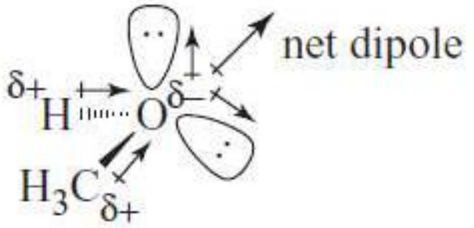
2.2

The shape of $CCl_2{=}CCl_2$ (below) is such that the vector sum of all of the C—Cl bond moments is zero.



2.3

VSEPR theory predicts the following.



2.4

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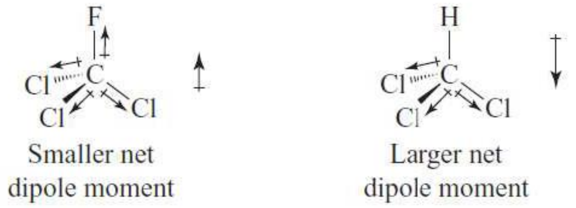
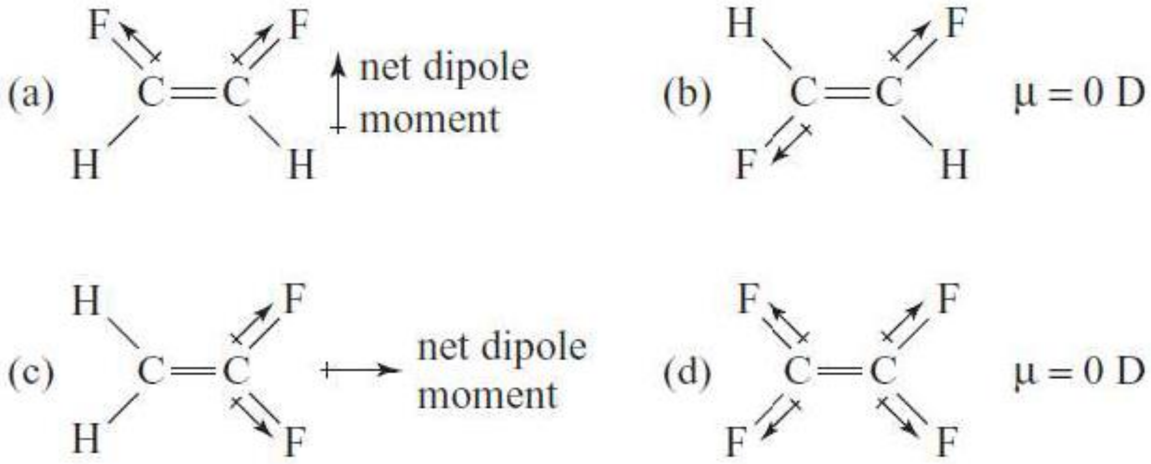
In $CFCl_3$ the large C—F bond moment opposes the C—Cl moments, leading to a net dipole moment in the direction of the fluorine. Because hydrogen is much less electronegative than fluorine, no such opposing effect occurs in $CHCl_3$; therefore, it has a net dipole moment that is larger and in the direction of the chlorine atoms.



2.5



2.6

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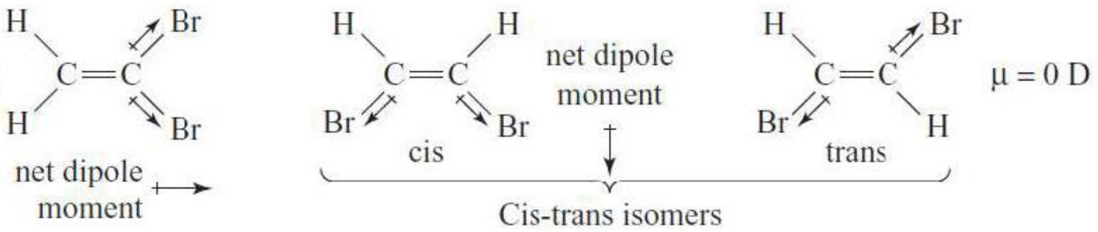
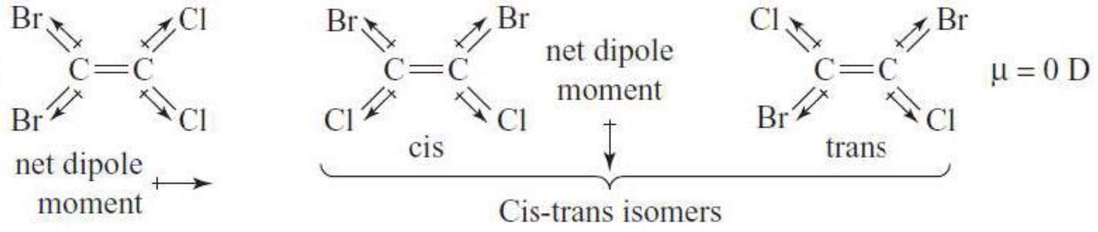
(a) 

(b) 

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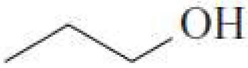
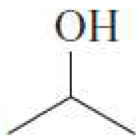
(a) 

(b) 

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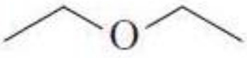
2.8

(a) 

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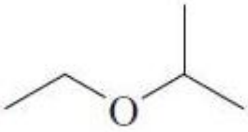
(c) 

(d) Methyl propyl ether

(e) Diisopropyl ether

(f) Methyl phenyl ether

2.9

(a) (e) only

(b) (a, c)

(c) (b, d, f, g)

2.10

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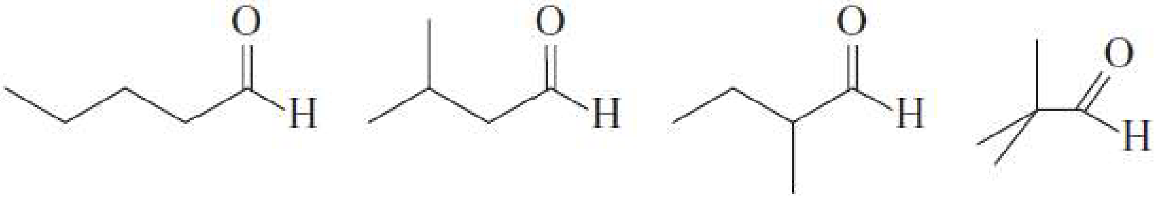
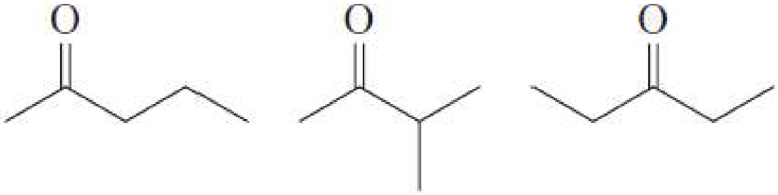
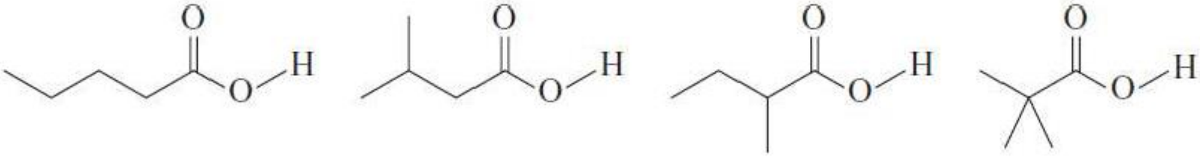
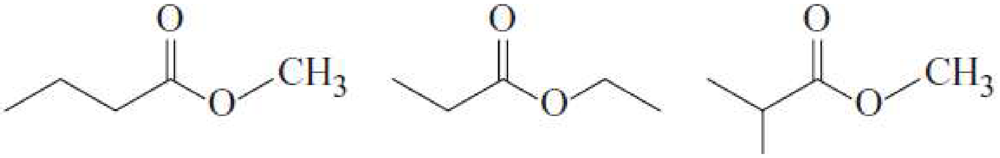
(a) 

(b) 

2.11



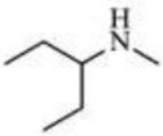
2.12

 + others

2.13

(a) greater capacity for intramolecular hydrogen bonding (2 -OH groups)

(b) alcohol vs. ether - -OH group capable of hydrogen bonding

(c)  greater capacity for intramolecular hydrogen bonding (-NH group)

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2.14

Cyclopropane would have the higher melting point because its cyclic structure gives it a rigid compact shape that would permit stronger crystal lattice forces.

2.15

d < a < b < c

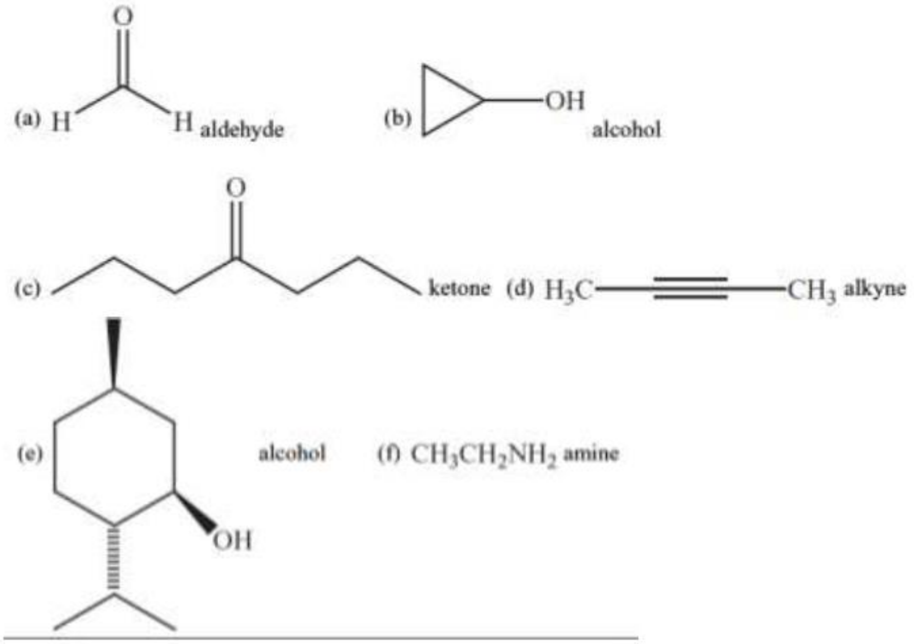
(c) has the highest boiling point due to hydrogen bonding involving its O—H group.

(b) is a polar molecule due to its C═O group, hence higher boiling than the essentially non-polar (a) and (d).

(a) has a higher boiling point than (d) because its unbranched structure permits more van der Waals attractions.

Review Problems

2.16



2.17

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(a) Three carbon-carbon double bonds (alkene) and a 2° alcohol

(b) Phenyl, carboxylic acid, amide, ester, and a 1° amine

(c) Phenyl and a 1° amine

(d) Carbon-carbon double bond and a 2° alcohol

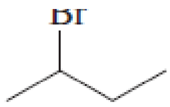
(e) Phenyl, ester, and a 3° amine

(f) Carbon-carbon double bond and an aldehyde

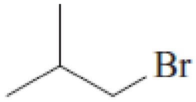
(g) Carbon-carbon double bond and 2 ester groups

2.18

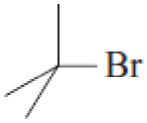
1° Alkyl bromide



2° Alkyl bromide

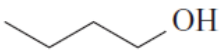


1° Alkyl bromide

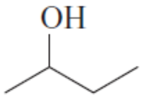


3° Alkyl bromide

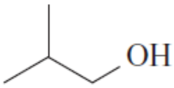
2.19



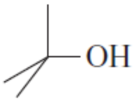
1° Alcohol



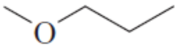
2° Alcohol



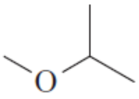
1° Alcohol



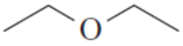
3° Alcohol



Ether



Ether



Ether

2.20

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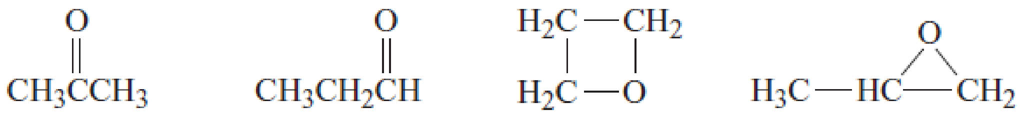
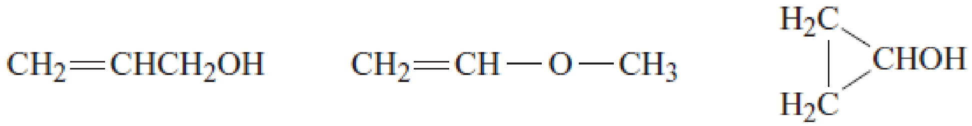
Any four of the following:



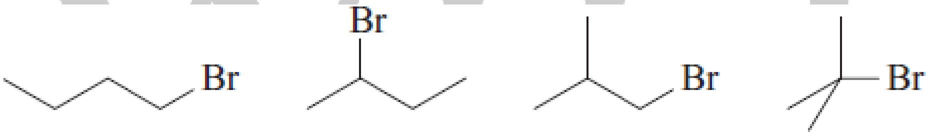
Ketone   Aldehyde   Ether   Ether



Alkene, alcohol   Alkene, ether   Alcohol

The ketone carbonyl absorption is in the 1680–1750 cm^{-1} range; that for the aldehyde is found in the 1690–1740 cm^{-1} region. The C—O absorption for the ethers is observed at about 1125 cm^{-1}. The C═C absorption occurs at approximately 1650 cm^{-1}. Absorption for the (hydrogen-bonded) O—H group takes the form of a broad band in the 3200–3550 cm^{-1} region.

2.21

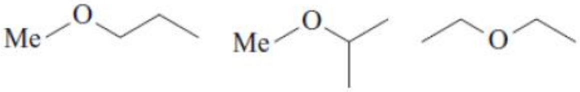


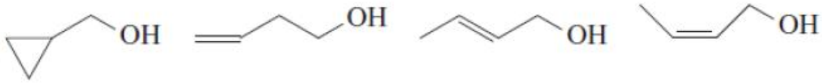
1° Alkyl bromide   2° Alkyl bromide   1° Alkyl bromide   3° Alkyl bromide

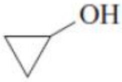
2.22

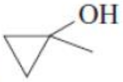
(a) 2°   (b) 1°   (c) 3°   (d) 2°   (e) 2°   (f) 3°

2.23

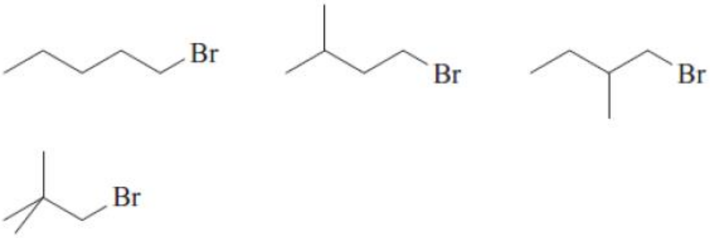
(a) 

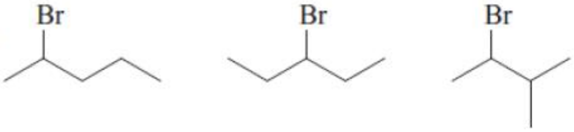
(b) 

(c) 

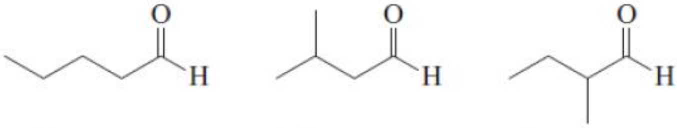
(d) 

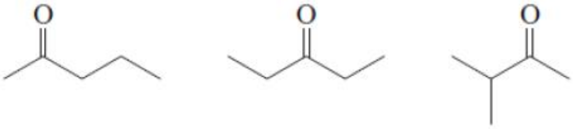
(e)

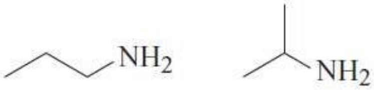
(f) 

(g) 

(h)

(i) 

(j) 

(k) 

(l)

(m) Me_3N

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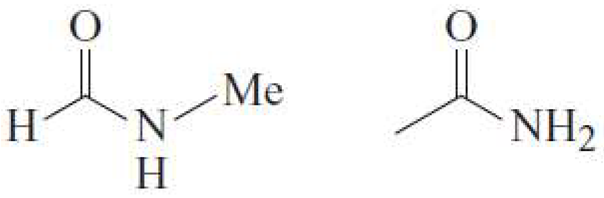
(n) 

2.24

The attractive forces between hydrogen fluoride molecules are the very strong dipole-dipole attractions that we call *hydrogen bonds*. (The partial positive charge of a hydrogen fluoride molecule is relatively exposed because it resides on the hydrogen nucleus. By contrast, the positive charge of an ethyl fluoride molecule is buried in the ethyl group and is shielded by the surrounding electrons. Thus the positive end of one hydrogen fluoride molecule can approach the negative end of another hydrogen fluoride molecule much more closely, with the result that the attractive force between them is much stronger.)

2.25

The cis isomer is polar while the trans isomer is nonpolar ($\mu = 0$ D). The intermolecular attractive forces are therefore greater in the case of the cis isomer, and thus its boiling point should be the higher of the two.

2.26

Because of its ionic character—it is a salt—the compound is water-soluble. The organic cation and the bromide ion are well-solvated by water molecules in a fashion similar to sodium bromide. The compound also is soluble in solvents of low polarity such as diethyl ether (though less so than in water). The hydrophobic alkyl groups can now be regarded as lipophilic—groups that seek a nonpolar environment. Attractive forces between the alkyl groups of different cations can be replaced, in part, by attractive dispersion forces between these alkyl groups and ether molecules.

2.27

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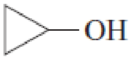
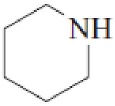
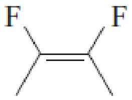
(a) because its molecules can form hydrogen bonds to each other through its $-\ddot{\underset{..}{O}}-H$ group.

(b) because with two $-\ddot{\underset{..}{O}}-H$ groups, its molecules can form more hydrogen bonds with each other.

(c) because its molecules can form hydrogen bonds to each other.

(d)  [same reason as (c)].

(e)  because its molecules can form hydrogen bonds to each other through the $-\ddot{N}-H$ group.

(f)  because its molecules will have a larger dipole moment. (The trans compound will have $\mu = 0$ D.)

2.28

(a) and (b) are polar and hence are able to dissolve ionic compounds. (c) and (d) are non-polar and will not dissolve ionic compounds.

2.29

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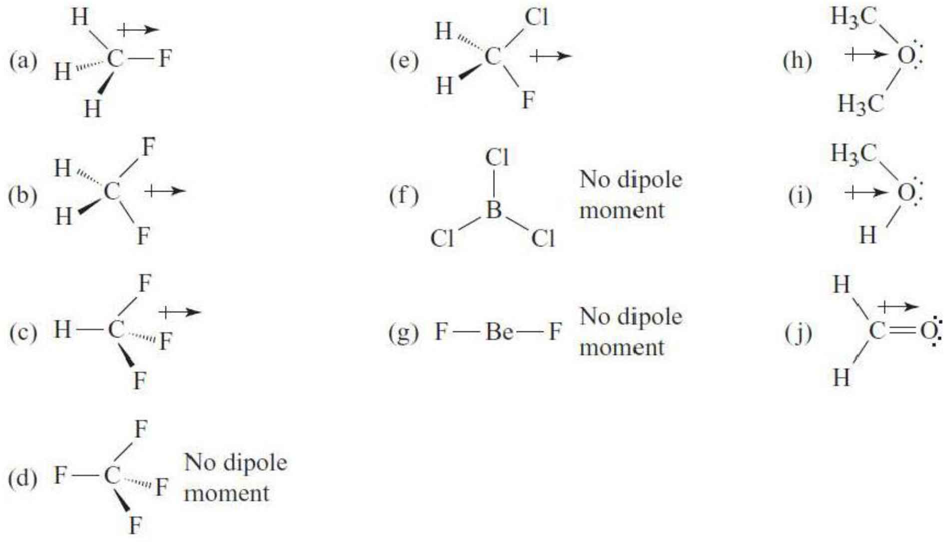
(a)
(b)
(c)
(d)
No dipole moment
(e)
(f)
No dipole moment
(g)
No dipole moment
(h)
(i)
(j)

2.30

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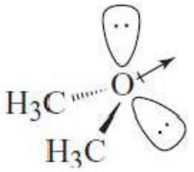
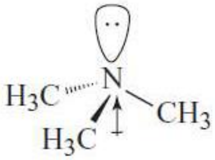
(a) Dimethyl ether: There are four electron pairs around the central oxygen: two bonding pairs and two nonbonding pairs. We would expect sp^3 hybridization of the oxygen with a bond angle of approximately 109.5° between the methyl groups.



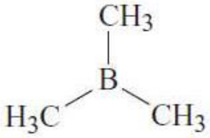
$\mu > 0$ D

(b) Trimethylamine: There are four electron pairs around the central nitrogen: three bonding pairs and one nonbonding pair. We would expect sp^3 hybridization of the nitrogen with a bond angle of approximately 109.5° between the methyl groups.



$\mu > 0$ D

(c) Trimethylboron: There are only three bonding electron pairs around the central boron. We would expect sp^2 hybridization of the boron with a bond angle of 120° between the methyl groups.



$\mu = 0$ D

(d) Dimethylberyllium: There are only two bonding electron pairs around the central beryllium atom. We would expect sp hybridization of the beryllium atom with a bond angle of 180° between the methyl groups.

$H_3C—Be—CH_3 \quad \mu = 0$ D

2.31

Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

2.32

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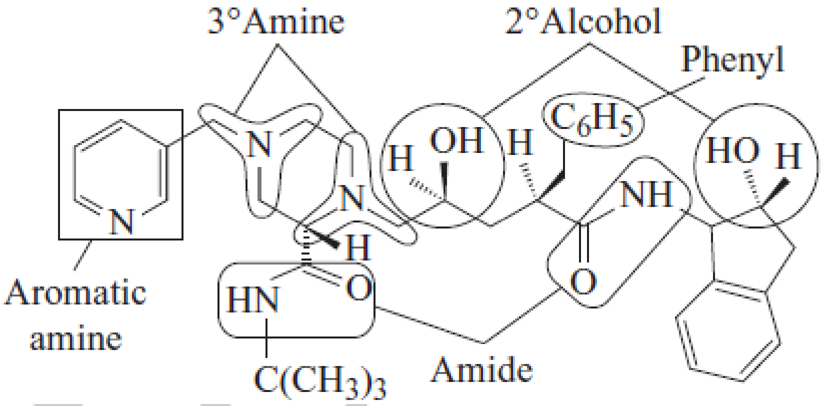
Without one (or more) polar bonds, a molecule cannot possess a dipole moment and, therefore, it cannot be polar. If the bonds are directed so that the bond moments cancel, however, the molecule will not be polar even though it has polar bonds.

2.33

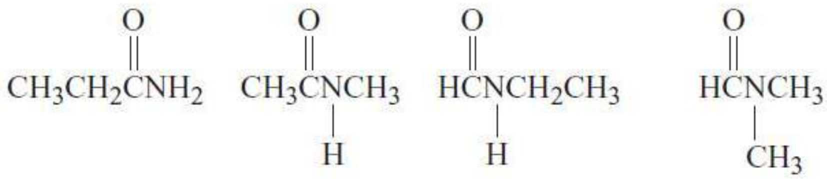
Crixivan has the following functional groups:



Multiconcept Problems

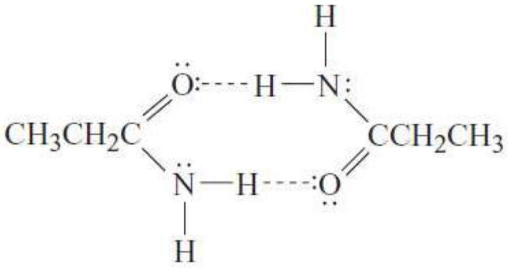
2.24

WILEY

(a) 

A B C D

(b) **D**, because it does not have a hydrogen that is covalently bonded to nitrogen and, therefore, its molecules cannot form hydrogen bonds to each other. The other molecules all have a hydrogen covalently bonded to nitrogen and, therefore, hydrogen-bond formation is possible. With the first molecule, for example, hydrogen bonds could form in the following way:



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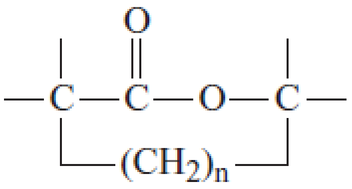
2.35



(a cyclic ester)

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (c) I and III are both the same molecules: 3,4-dimehtylhexane.

2. **(a)** Only ether functional group is present.

3. **(d)** Longer the hydrophobic alkyl part, lesser is the solubility.

4. **(b)** Alcohol (R-OH), Ether (R-O-R), Ketone (R-CO-R) and alkene (C=C) are all present.

5. **(c)** More the branching and lesser the mass, lesser is the boiling point due to decreased surface area and thus lesser Van Der Waal's attraction.

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6. **(a)** Secondary carbon atom is one which is directly attached to two other C atoms.

7. **(a)** CH_3F has the greatest dipole due to the highest electronegativity of F which results is greater charge generation.

8. **(b)** Functional groups present are alkyne, alkene, ketone and carboxylic acid.

<H2> Integer Type

1. (8) Functional groups present are: amide, amine, ketone, alcohol, alkene, carboxylic acid, aldehyde, ester.

2. **(21)** Secondary carbon atom is one which is directly attached to two other C atoms.

<H2> **Matrix Match Type**

1. a→(q),(s),(t) ,b→(p),(s),(t); c→(q),(r),(s) ; d→(p), (q), (r), (s), (t)

Degree of amine is defined as the number of C atoms directly attached to the N atom of amine, while the degree of C is defined as the number of C atoms directly attached to the C atom.

2. a→(p),(r),(s) ; b→(q),(r) ; c→(q),(r) ; d→(p), (r), (s)

Melting point is determined on the basis of packing efficiency which is greater for the trans isomer than the cis isomer, higher the packing efficiency higher is the melting point. Boiling point is determined on the basis of dipole, higher the dipole higher is the boiling point.

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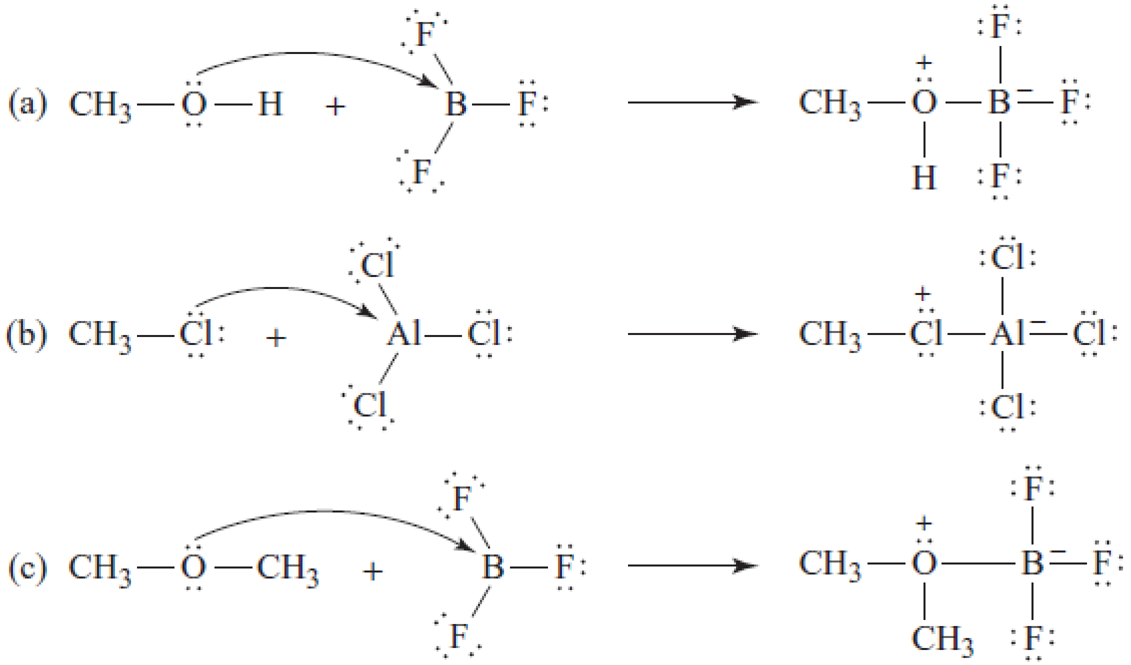
Chapter 3: An Introduction to Organic reactions and Their Mechanisms: Acids and Bases

Practice Problems

3.1



3.2

(a) Lewis base

(b) Lewis acid

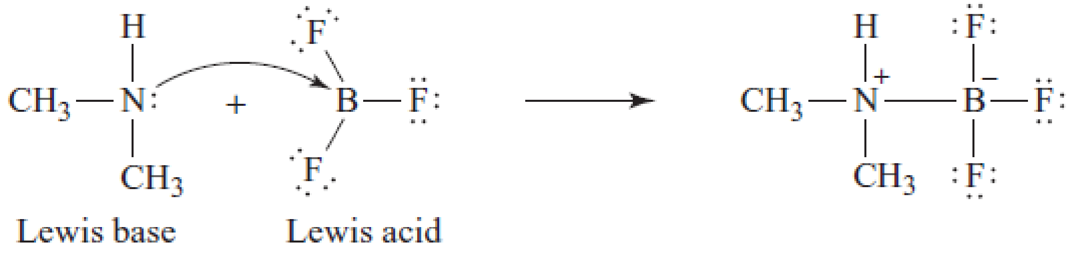
(c) Lewis base

(d) Lewis base

(e) Lewis acid

(f) Lewis base

3.3



3.5

Nucleophile, Electrophile, Nucleophile, Nucleophile, Electrophile, Nucleophile

3.7

(a) $K_a = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = 1.77 \times 10^{-4}$

Let $x = [H_3O^+] = [HCO_2^-]$ at equilibrium

then, $0.1 - x = [HCO_2H]$ at equilibrium

but, since the K_a is very small, x will be very small and $0.1 - x \simeq 0.1$

Therefore,

$$\frac{(x)(x)}{0.1} = 1.77 \times 10^{-4}$$

$$x^2 = 1.77 \times 10^{-5}$$

$$x = 0.0042 = [H_3O^+] = [HCO_2^-]$$

(b) $\% \text{ Ionized} = \frac{[H_3O^+]}{0.1} \times 100 \quad \text{or} \quad \frac{[HCO_2^-]}{0.1} \times 100$

$$= \frac{.0042}{0.1} \times 100 = 4.2\%$$

3.8

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(a) $pK_a = -\log 10^{-7} = -(-7) = 7$

(b) $pK_a = -\log 5.0 = -0.7$

(c) Since the acid with a $K_a = 5$ has a larger K_a, it is the stronger acid.

3.9

STRATEGY AND ANSWER: When H_3O^+ acts as an acid in aqueous solution, the equilibrium is

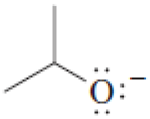
$$H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$$

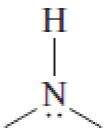
and K_a is equal to the molar concentration of water;

$$K_a = \frac{[H_2O][H_3O^+]}{[H_3O^+]} = [H_2O]$$

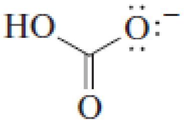
The molar concentration of H_2O in pure H_2O is equal to the number of moles of H_2O (MW = 18 g/mol) in 1000 g (one liter) of water. That is, $[H_2O] = 1000\text{ g L}^{-1}/18\text{ g/mole}^{-1} = 55.5$. Therefore, $K_a = 55.5$. The $pK = -\log 55.5 = -1.74$.

3.10

(a) 

(c) 

(b)

(d) 

3.11

The pK_a of the methylaminium ion is equal to 10.6 (Section 3.6C). Since the pK_a of the anilinium ion is equal to 4.6, the anilinium ion is a stronger acid than the methylaminium ion, and aniline ($C_6H_5NH_2$) is a weaker base than methylamine (CH_3NH_2).

3.12

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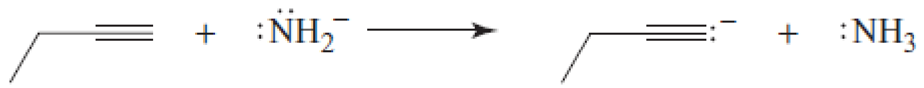


3.13

(a) Negative. Because the atoms are constrained to one molecule in the product, they have to become more ordered.

(b) Approximately zero.

(c) Positive. Because the atoms are in two separate product molecules, they become more disordered.

3.14

(a) If $K_{eq} = 1$

then,

$$\log\ K_{eq} = 0 = \frac{-\Delta G^\circ}{2.303RT}$$

$$\Delta G^\circ = 0$$

(b) If $K_{eq} = 10$

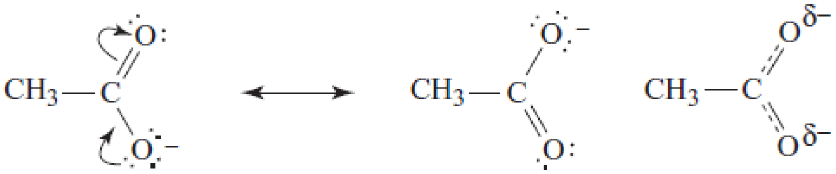
then,

$$\log K_{eq} = 1 = \frac{-\Delta G^\circ}{2.303RT}$$

$$\Delta G^\circ = -(2.303)(0.008314\ \text{kJ mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) = -5.71\ \text{kJ mol}^{-1}$$

3.15

Structures **A** and **B** make equal contributions to the overall hybrid. This means that the carbon-oxygen bonds should be the same length and that the oxygens should bear equal negative charges.



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3.16

(a) $CHCl_2CO_2H$ would be the stronger acid because the electron-withdrawing inductive effect of *two chlorine atoms* would make its hydroxyl proton more positive. The electron-withdrawing effect of the two chlorine atoms would also stabilize the dichloroacetate ion more effectively by dispersing its negative charge more extensively.

(b) CCl_3CO_2H would be the stronger acid for reasons similar to those given in (a), except here there are three versus two electron-withdrawing chlorine atoms involved.

(c) CH_2FCO_2H would be the stronger acid because the electron-withdrawing effect of a fluorine atom is greater than that of a bromine atom (fluorine is more electronegative).

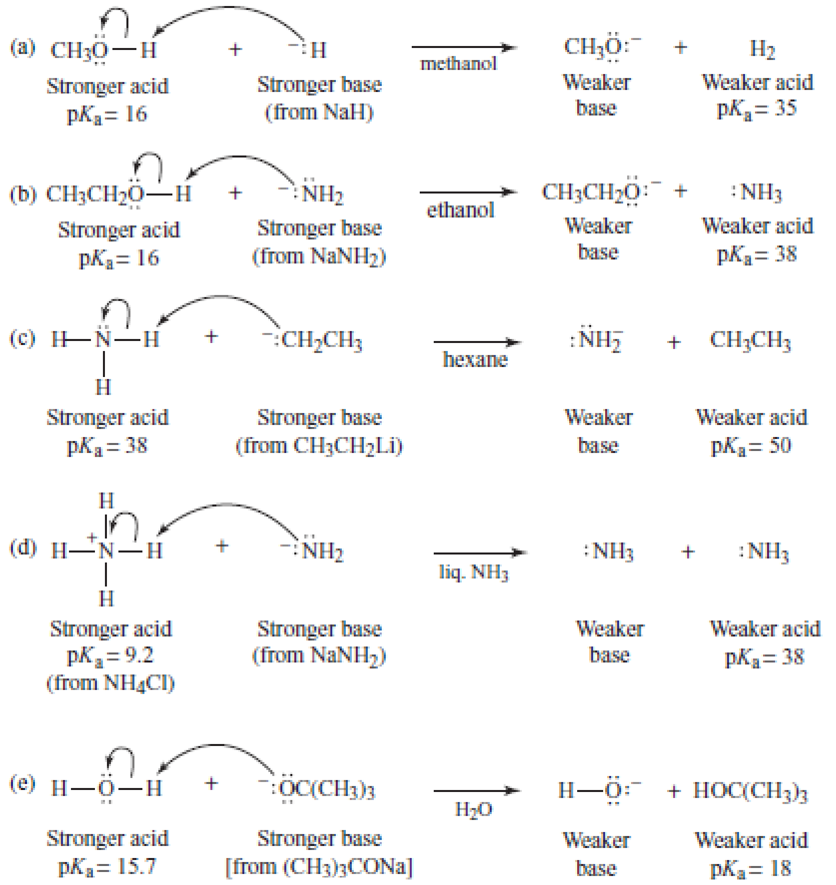
(d) CH_2FCO_2H is the stronger acid because the fluorine atom is nearer the carboxyl group and is, therefore, better able to exert its electron-withdrawing inductive effect. (*Remember:*

Inductive effects weaken steadily as the distance between the substituent and the acidic group increases.)

3.17

All compounds containing oxygen and most compounds containing nitrogen will have an unshared electron pair on their oxygen or nitrogen atom. These compounds can, therefore, act as bases and accept a proton from concentrated sulfuric acid. When they accept a proton, these compounds become either oxonium ions or ammonium ions, and having become ionic, they are soluble in the polar medium of sulfuric acid. The only nitrogen compounds that do not have an electron pair on their nitrogen atom are quaternary ammonium compounds, and these, already being ionic, also dissolve in the polar medium of concentrated sulfuric acid.

3.18



(f) No appreciable acid-base reaction would occur because HO^- is not a strong enough base to remove a proton from $(CH_3)_3COH$.

3.19

(a) $HC{\equiv}CH + NaH \xrightarrow{\text{hexane}} HC{\equiv}CNa + H_2$

(b) $HC{\equiv}CNa + D_2O \longrightarrow HC{\equiv}CD + NaOD$

(c) $CH_3CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2D + LiOD$

(d) $CH_3CH_2OH + NaH \xrightarrow{\text{hexane}} CH_3CH_2ONa + H_2$

(e) $CH_3CH_2ONa + T_2O \longrightarrow CH_3CH_2OT + NaOT$

(f) $CH_3CH_2CH_2Li + D_2O \xrightarrow{\text{hexane}} CH_3CH_2CH_2D + LiOD$

Review Problems

Bronsted–Lowry Acids and Bases

3.20

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(a) $^{-}\!:\ddot{N}H_2$ (the amide ion)

(b) $H—\ddot{\underset{..}{O}}:^{-}$ (the hydroxide ion)

(c) $:H^{-}$ (the hydride ion)

(d) $H—C \equiv C:^{-}$ (the ethynide ion)

(e) $CH_3\ddot{\underset{..}{O}}:^{-}$ (the methoxide ion)

(f) $H_2\ddot{\underset{..}{O}}$ (water)

3.21

$$^{-}\!:\ddot{N}H_2 > :H^{-} > H—C \equiv C:^{-} > CH_3\ddot{\underset{..}{O}}:^{-} \approx H—\ddot{\underset{..}{O}}:^{-} > H_2O$$

3.22

(a) H_2SO_4

(b) H_3O^+

(c) $CH_3NH_3^+$

(d) NH_3

(e) CH_3CH_3

(f) CH_3CO_2H

3.23

$$H_2SO_4 > H_3O^+ > CH_3CO_2H > CH_3NH_3^+ > NH_3 > CH_3CH_3$$

Lewis Acids and Bases

3.24

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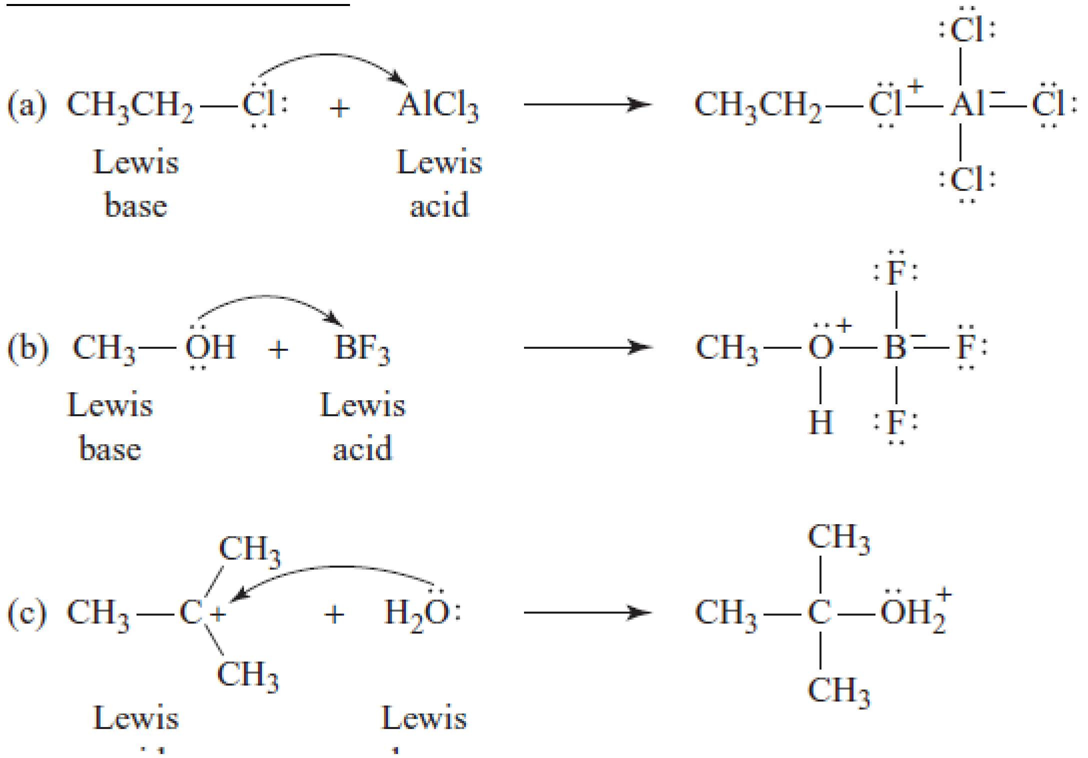
Lewis Acids and Bases



Curved-Arrow Notation

3.25

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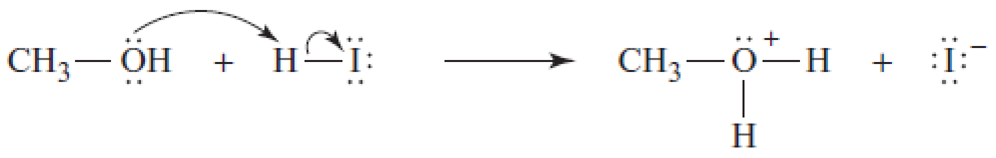
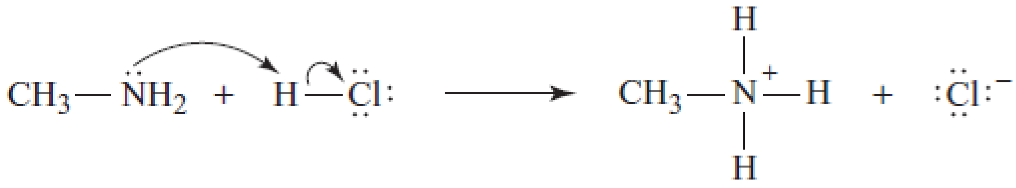
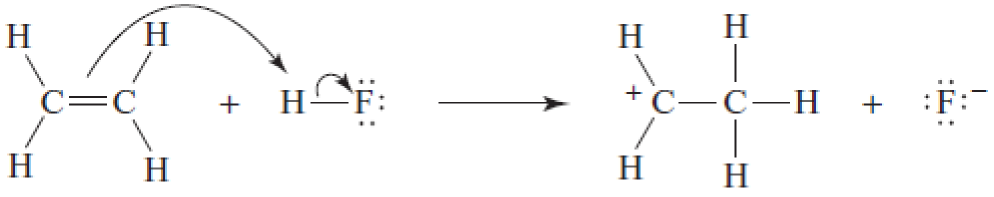
(a) 

(b) 

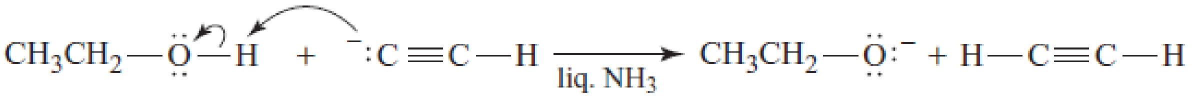
(c) 

Acid–Base Strength and Equilibria

3.26

Because the proton attached to the highly electronegative oxygen atom of CH_3OH is much more acidic than the protons attached to the much less electronegative carbon atom.

3.27



3.28

(a) $pK_a = -\log 1.77 \times 10^{-4} = 4 - 0.248 = 3.75$

(b) $K_a = 10^{-13}$

3.29

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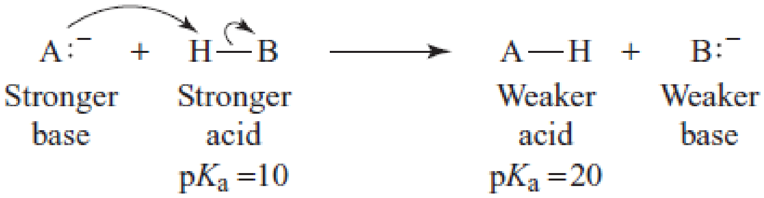
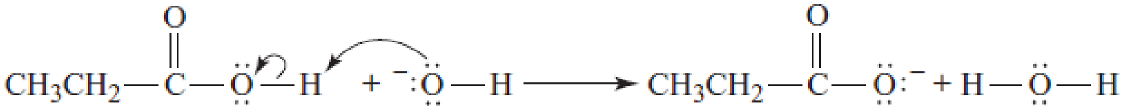
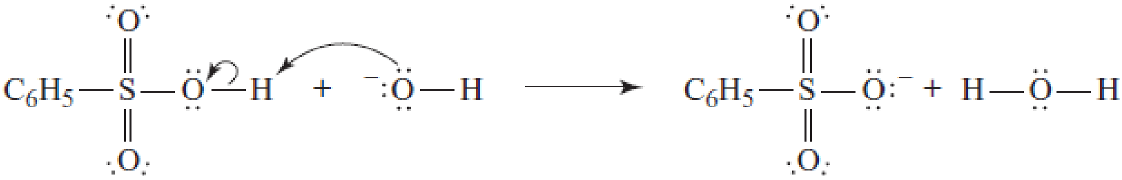
(a) HB is the stronger acid because it has the smaller pK_a.

(b) Yes. Since A^- is the stronger base and HB is the stronger acid, the following acid-base reaction will take place.

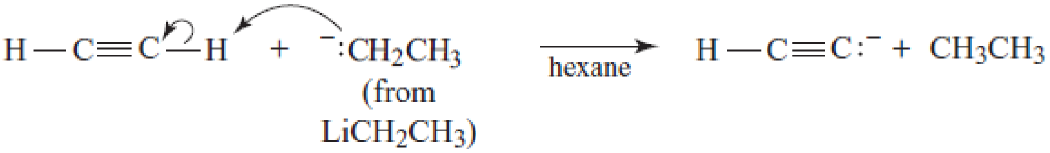


3.30

(a) 

(b) 

(c) No appreciable acid-base reaction takes place because CH_3CH_2ONa is too weak a base to remove a proton from ethyne.

(d) 

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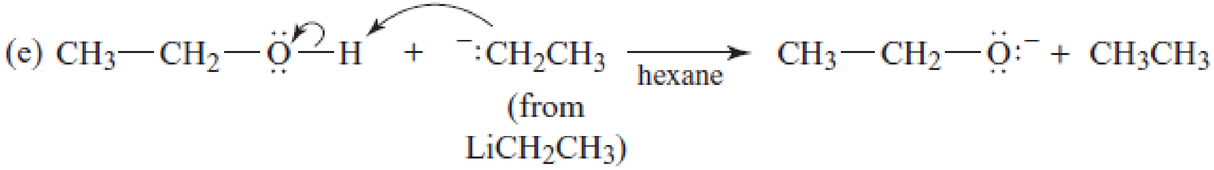

3.31

(a) $C_6H_5{-}C{\equiv}C{-}H + NaNH_2 \xrightarrow{\text{ether}} C_6H_5{-}C{\equiv}C{:}^- \; Na^+ + NH_3$

then

$C_6H_5{-}C{\equiv}C{:}^- \; Na^+ + T_2O \longrightarrow C_6H_5{-}C{\equiv}C{-}T + NaOT$

(b) $CH_3{-}CH(CH_3){-}O{-}H + NaH \longrightarrow CH_3{-}CH(CH_3){-}O^- \, Na^+ + H_2$

then

$CH_3{-}CH(CH_3){-}O^- \, Na^+ + D_2O \longrightarrow CH_3{-}CH(CH_3){-}O{-}D + NaOD$

(c) $CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2O^- \, Na^+ + H_2$

then

$CH_3CH_2CH_2O^- \, Na^+ + D_2O \longrightarrow CH_3CH_2CH_2OD + NaOD$

3.32

(a) $CH_3CH_2OH > CH_3CH_2NH_2 > CH_3CH_2CH_3$

Oxygen is more electronegative than nitrogen, which is more electronegative than carbon. The O-H bond is most polarized, the N-H bond is next, and the C-H bond is least polarized.

(b) $CH_3CH_2O^- < CH_3CH_2NH^- < CH_3CH_2CH_2^-$

The weaker the acid, the stronger the conjugate base.

3.33

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(a) $CH_3C{\equiv}CH$ > $CH_3CH{=}CH_2$ > $CH_3CH_2CH_3$

(b) $CH_3CHClCO_2H$ > $CH_3CH_2CO_2H$ > $CH_3CH_2CH_2OH$

(c) $CH_3CH_2OH_2^+$ > CH_3CH_2OH > CH_3OCH_3

3.34

(a) $CH_3NH_3^+$ < CH_3NH_2 < CH_3NH^-

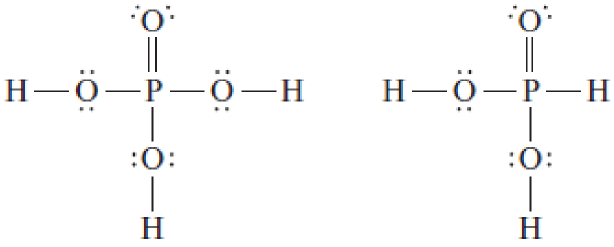
(b) CH_3O^- < CH_3NH^- < $CH_3CH_2^-$

(c) $CH_3C{\equiv}C^-$ < $CH_3CH{=}CH^-$ < $CH_3CH_2CH_2^-$

General Problems

3.35

The acidic hydrogens must be attached to oxygen atoms. In H_3PO_3, one hydrogen is bonded to a phosphorus atom:



3.36

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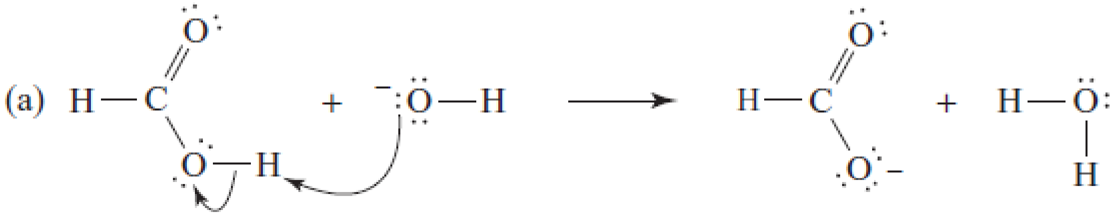

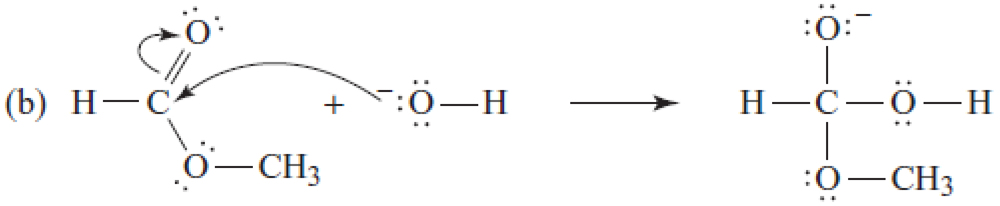

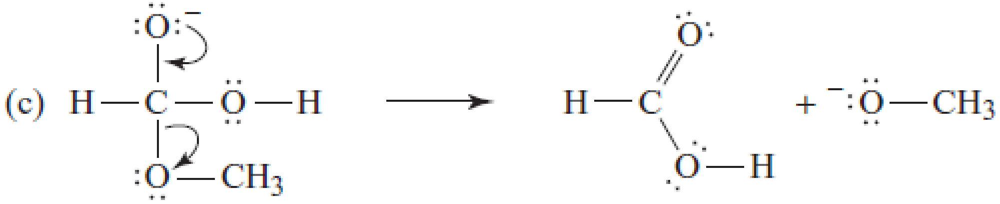

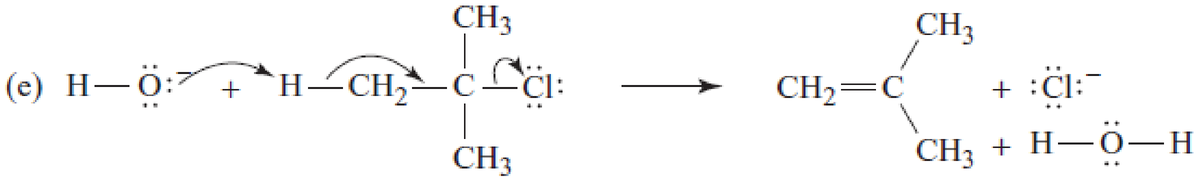

3.37

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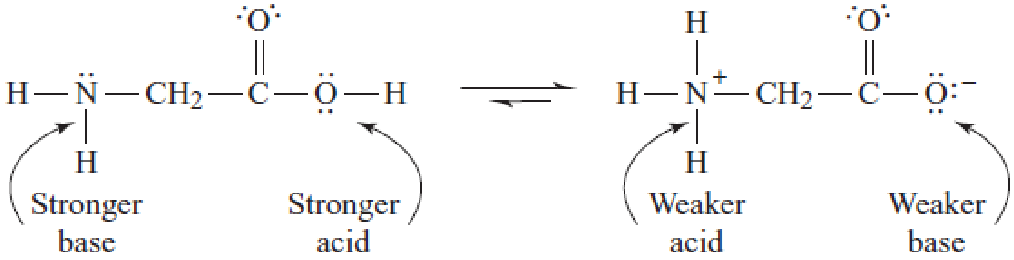
(a) Assume that the acidic and basic groups of glycine in its two forms have acidities and basicities similar to those of acetic acid and methylamine. Then consider the equilibrium between the two forms:



We see that the ionic form contains the groups that are the weaker acid and weaker base. The equilibrium, therefore, will favor this form.

(b) The high melting point shows that the ionic structure better represents glycine.

3.38

(a) The second carboxyl group of malonic acid acts as an electron-withdrawing group and stabilizes the conjugate base formed (i.e., $HO_2CCH_2CO_2^-$) when malonic acid loses a proton. [Any factor that stabilizes the conjugate base of an acid always increases the strength of the acid (Section 3.11C).] An important factor here may be an entropy effect as explained in Section 3.10.

(b) When $^-O_2CCH_2CO_2H$ loses a proton, it forms a dianion, $^-O_2CCH_2CO_2^-$. This dianion is destabilized by having two negative charges in close proximity.

3.39

HB is the stronger acid.

3.40

$$\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= 6.3 \text{ kJ mol}^{-1} - (298 \text{ K})(0.0084 \text{ kJ mol}^{-1}\text{K}^{-1}) \\
&= 3.8 \text{ kJ mol}^{-1} \\
\log K_{eq} &= \log K_a = -pK_a = -\frac{\Delta G^\circ}{2.303RT} \\
pK_a &= \frac{\Delta G^\circ}{2.303RT} \\
pK_a &= \frac{3.8 \text{ kJ mol}^{-1}}{(2.303)(0.008314 \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})} \\
pK_a &= 0.66
\end{aligned}$$

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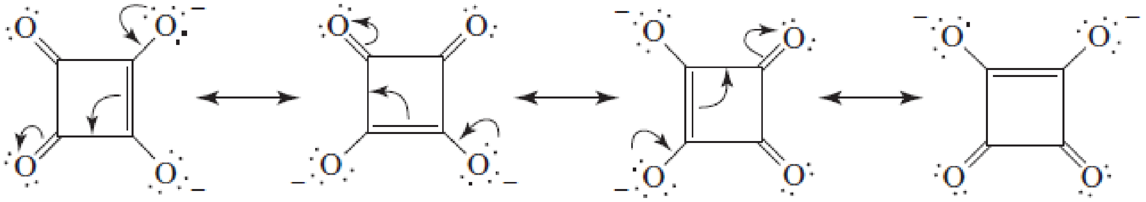
3.41

The dianion is a hybrid of the following resonance structures:



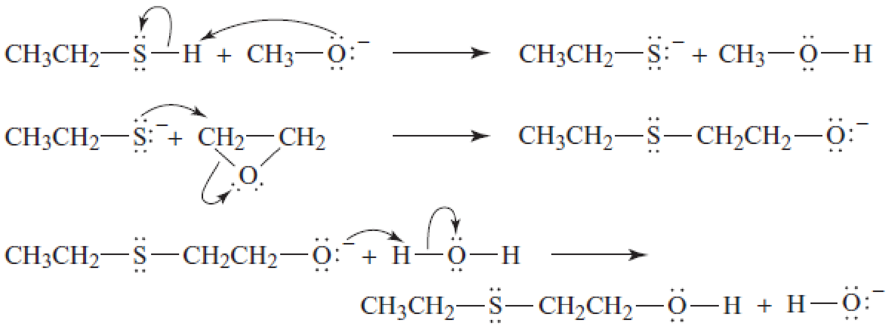
3.42

(a) A is $CH_3CH_2S^-$ B is CH_3OH

C is $CH_3CH_2SCH_2CH_2O^-$ D is $CH_3CH_2SCH_2CH_2OH$

E is OH^-

(b)



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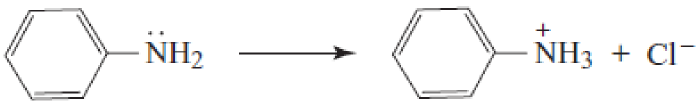
3.43

(a) $CH_3(CH_2)_8OD + CH_3(CH_2)_8Li \longrightarrow CH_3(CH_2)_8O^- \ Li^+ + CH_3(CH_2)_8D$

Hexane could be used as solvent. Liquid ammonia and ethanol could not because they would compete with $CH_3(CH_2)_8OD$ and generate mostly non-deuterio-labelled $CH_3(CH_2)_7CH_3$.

(b) $NH_2^- + CH_3C{\equiv}CH \longrightarrow NH_3 + CH_3C{\equiv}C{:}^-$

Hexane or liquid ammonia could be used; ethanol is too acidic and would lead to $CH_3CH_2O^-$ (ethoxide ion) instead of the desired alkynide ion.

(c) HCl + 

Hexane or ethanol could be used; liquid ammonia is too strong a base and would lead to NH_4^+ instead of the desired anilinium ion.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (b) Order of electronegativity is $sp > sp^2 > sp^3$.

2. (d) More the –I effect, greater is the acidic strength. The –I strength depends upon electronegativity and distance.

3. (c) Conjugate anion of II is stabilized by resonance from two sides, that of I is resonance stabilized only from one side and conjugate of III is not resonance stabilized.
4. (c) Greater the –I effect, greater is the acidic strength.
5. **(b)** The limited two moles of the base $NaNH_2$ would remove the two most acidic H atoms of the molecule which are from the Sulfonic acid and the carboxylic acid respectively.

6. (d) The *sp* carbon atom is more electronegative than the sp^3 carbon, thus it has a more stable conjugate base (anion), which causes its acidic strength to be higher.

7. (c) Largest p*K*a means the weakest acid. Ester is the weakest acid of the given molecules as its conjugate is the least stabilized due to effective resonance between the oxygen atoms

8. (d) Both the acids result in the release of CO_2 gas as acids stronger than H_2CO_3 react with $NaHCO_3$ to release CO_2 gas.
9. (c) Acidic strength order is based on the order of stability of conjugate base.

10. (b) Most acidic as its conjugate base (anion) is the most stabilized due to resonance.

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11. (d) Active methylene H atom present between two keto groups is acidic due to resonance stabilization from two sides.

12. (b) Since O is the most electronegative, its conjugate base with negative charge on O is the most stable.
13. (a) Most acidic due to strong –I and –M effect of the nitro group.

14. (c) Electron withdrawing group decreases the basic strength. The nitro group at *meta* has lesser electron withdrawing effect than nitro group at para as per its resonance structure.

15. (a) More the electron donating tendency more is the basic strength. Anions have greater electron donating tendency generally than neutral molecules.
16. (a) Only in (a) the lone pair of N atom is not involved in resonance, thus it is more readily available for donation.

<H2> **Integer Type**
1. (2) $NaHCO_3$ will only react with species more acidic than H_2CO_3 which in this molecule are the carboxylic and the sulfonic acid groups only.

<H2> **Matrix Match Type**

1. a→(s); b→(r); C→(q); D→(p)
Lesser the pKa, more is the acidic strength. Acidic strength increases with –I effect as in B and C (ammonium group) and decreases with +I effect as in D (carboxylate anion).

2. **a→(r); b→(q); c→(s); d→(p)**
In A and B, Sodium bicarbonate will react with the carboxylic acid to release CO_2 gas with the C coming from $NaHCO_3$. In C, Na (active metal) reacts with acid to release H_2 has while in D, the base $NaNH_2$ will abstract proton from the acid to release NH_3 gas.

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Chapter 4: Stereochemistry: Chiral Molecules

Practice Problems

4.1

(a) Achiral
(b) Achiral
(c) Chiral
(d) Chiral
(e) Chiral
(f) Chiral
(g) Chiral
(h) Achiral

4.2

(a) Yes
(b) No
(c) No

4.3

(a) They are the same molecule.
(b) They are enantiomers.

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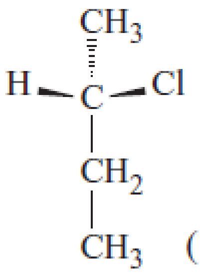
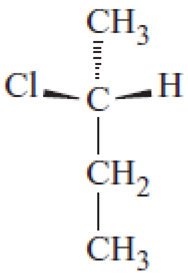
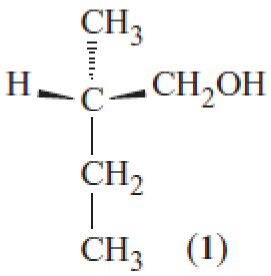
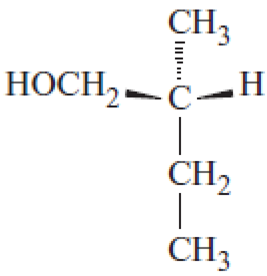
4.4

(a), (b), (e), (g), and (i) do not have chirality centers.

(c)  (1)

 (2)

(d)  (1)

 (2)

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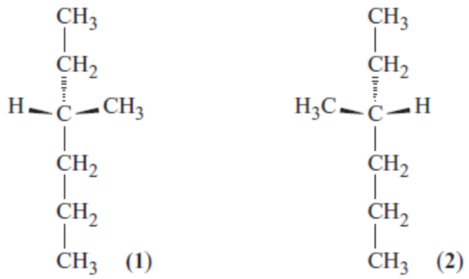
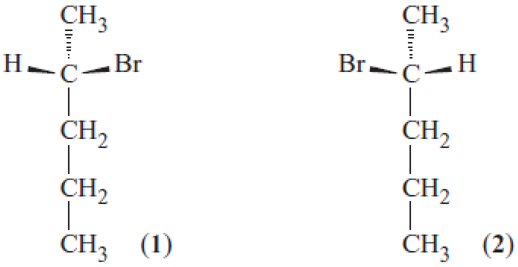
(h) 

(f) 

(j)

4.5

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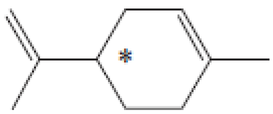
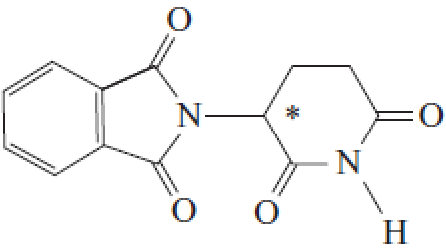
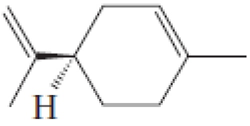
(a) 

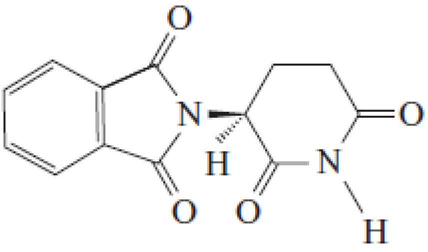
Limonene

(b) 

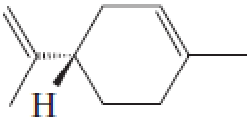
Thalidomide



(*R*)



(*S*)



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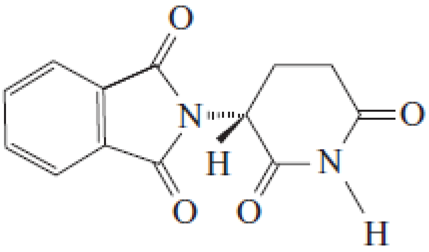

(*R*)

4.6

The following items possess a plane of symmetry, and are, therefore, achiral.

(a) A screwdriver

(b) A baseball bat (ignoring any writing on it)

(h) A hammer

4.7

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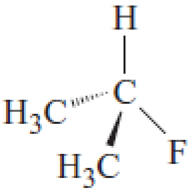
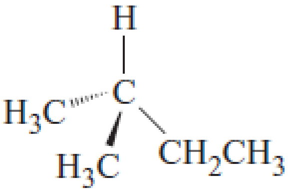
In each instance below, the plane defined by the page is a plane of symmetry.

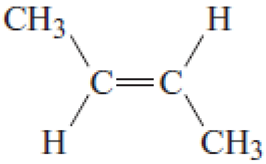
(a)



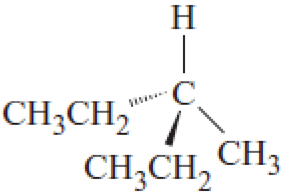
(b)



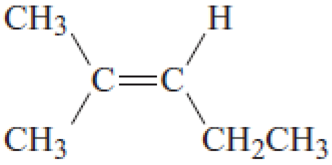
(e)



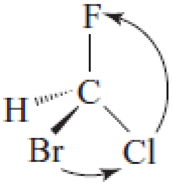
(g)



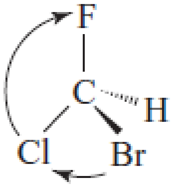
(i)



4.8



(*S*)



(*R*)

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4.9

(c) (1) is (*S*)
(2) is (*R*)

(d) (1) is (*S*)
(2) is (*R*)

(f) (1) is (*S*)
(2) is (*R*)

(h) (1) is (*S*)
(2) is (*R*)

(j) (1) is (*S*)
(2) is (*R*)

4.10

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(a) —Cl > —SH > —OH > —H

(b) $—CH_2Br$ > $—CH_2Cl$ > $—CH_2OH$ > $—CH_3$

(c) —OH > —CHO > $—CH_3$ > —H

(d) $—C(CH_3)_3$ > $—CH{=}CH_2$ > $—CH(CH_3)_2$ > —H

(e) $—OCH_3$ > $—N(CH_3)_2$ > $—CH_3$ > —H

(f) $—OPO_3H_2$ > —OH > —CHO > —H

4.11

(a) (*S*) (b) (*R*) (c) (*S*) (d) (*R*)

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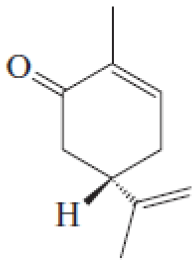
4.12

(a) Enantiomers

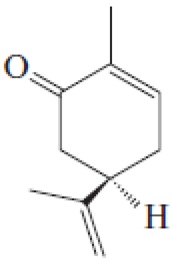
(b) Two molecules of the same compound

(c) Enantiomers

4.13



(*S*)-(+)-Carvone



(*R*)-(–)-Carvone

4.14

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(a) $$\text{Enant. excess} = \frac{\text{observed specific rotation}}{\text{specific rotation of pure enantiomer}} \times 100$$

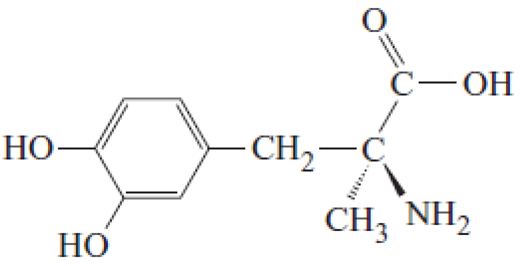
$$= \frac{+1.151}{+5.756} \times 100$$

$$= 20.00\%$$

(b) Since the (*R*) enantiomer (see Section 5.8C) is +, the (*R*) enantiomer is present in excess.

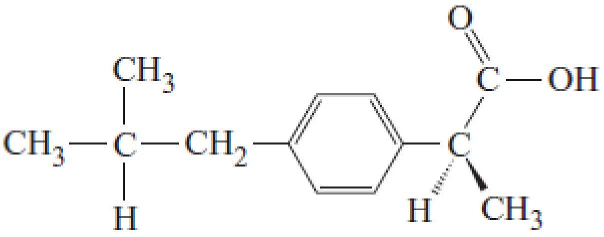
4.15

(a)



(*S*)-Methyldopa

(c)



(*S*)-Ibuprofen

4.16

(a) Diastereomers.

(b) Diastereomers in each instance.

(c) No, diastereomers have different melting points.

(d) No, diastereomers have different boiling points.

(e) No, diastereomers have different vapor pressures.

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4.17

(a) Diastereomers.

(b) Diastereomers in each instance.

(c) No, diastereomers have different melting points.

(d) No, diastereomers have different boiling points.

(e) No, diastereomers have different vapor pressures.

4.18

(a) Represents **A**

(b) Represents **C**

(c) Represents **B**

4.19

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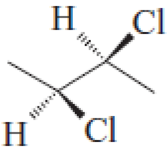
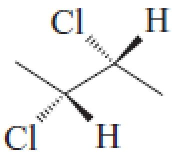
(a)

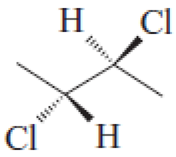


(1)



(2)

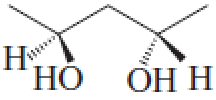
Enantiomers



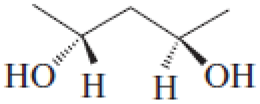
(3)

Meso compound

(b)

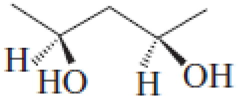


(1)



(2)

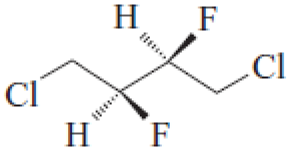
Enantiomers



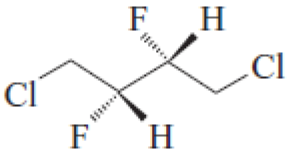
(3)

Meso compound

(c)

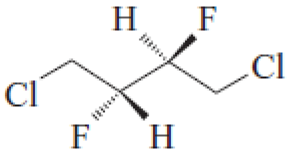


(1)



(2)

Enantiomers



(3)

Meso compound

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(d)

(1) (2) (3) (4)

Enantiomers Enantiomers

(e)

(1) (2) (3) (4)

Enantiomers Enantiomers

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4.20

B is (2*S*,3*S*)-2,3-Dibromobutane
C is (2*R*,3*S*)-2,3-Dibromobutane

4.21

(a) (1) is (2*S*,3*S*)-2,3-Dichlorobutane
(2) is (2*R*,3*R*)-2,3-Dichlorobutane
(3) is (2*R*,3*S*)-2,3-Dichlorobutane

(b) (1) is (2*S*,4*S*)-2,4-Pentanediol
(2) is (2*R*,4*R*)-2,4-Pentanediol
(3) is (2*R*,4*S*)-2,4-Pentanediol

(c) (1) is (2*R*,3*R*)-1,4-Dichloro-2,3-difluorobutane
(2) is (2*S*,3*S*)-1,4-Dichloro-2,3-difluorobutane
(3) is (2*R*,3*S*)-1,4-Dichloro-2,3-difluorobutane

(d) (1) is (2*S*,4*S*)-4-Chloro-2-pentanol
(2) is (2*R*,4*R*)-4-Chloro-2-pentanol
(3) is (2*S*,4*R*)-4-Chloro-2-pentanol
(4) is (2*R*,4*S*)-4-Chloro-2-pentanol

(e) (1) is (2*S*,3*S*)-2-Bromo-3-fluorobutane
(2) is (2*R*,3*R*)-2-Bromo-3-fluorobutane
(3) is (2*S*,3*R*)-2-Bromo-3-fluorobutane
(4) is (2*R*,3*S*)-2-Bromo-3-fluorobutane

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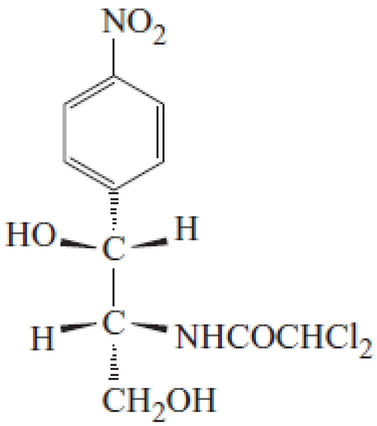
4.22



Chloramphenicol

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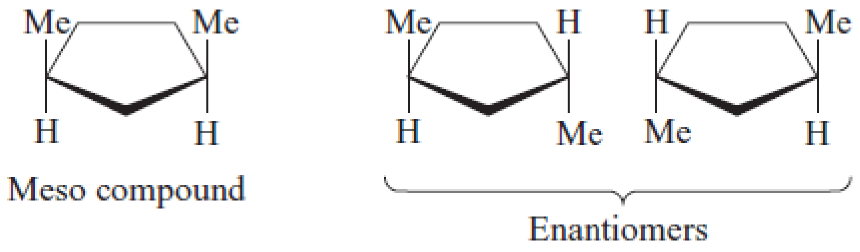
4.23

(a) No (b) Yes (c) No (d) No (e) Diastereomers

(f) Diastereomers

4.24



4.25

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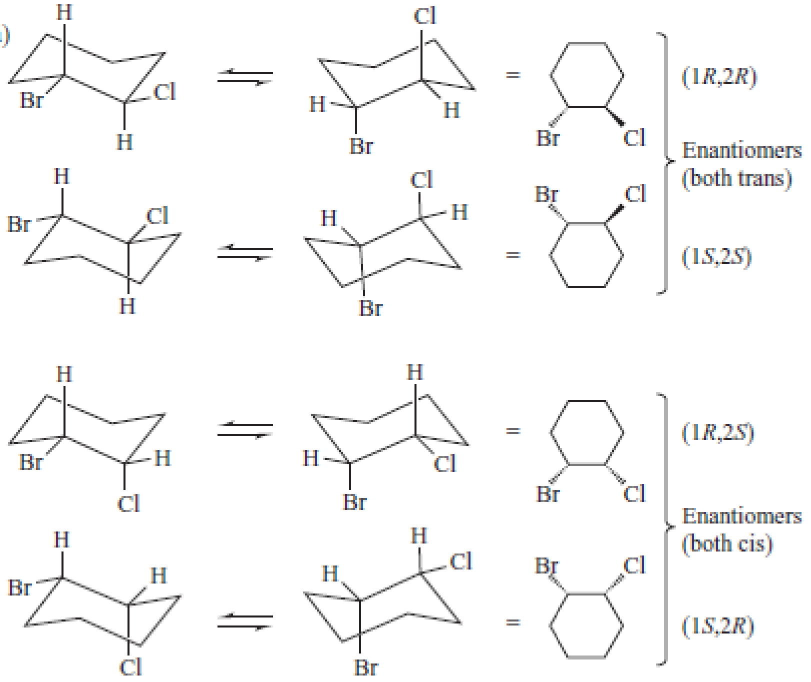
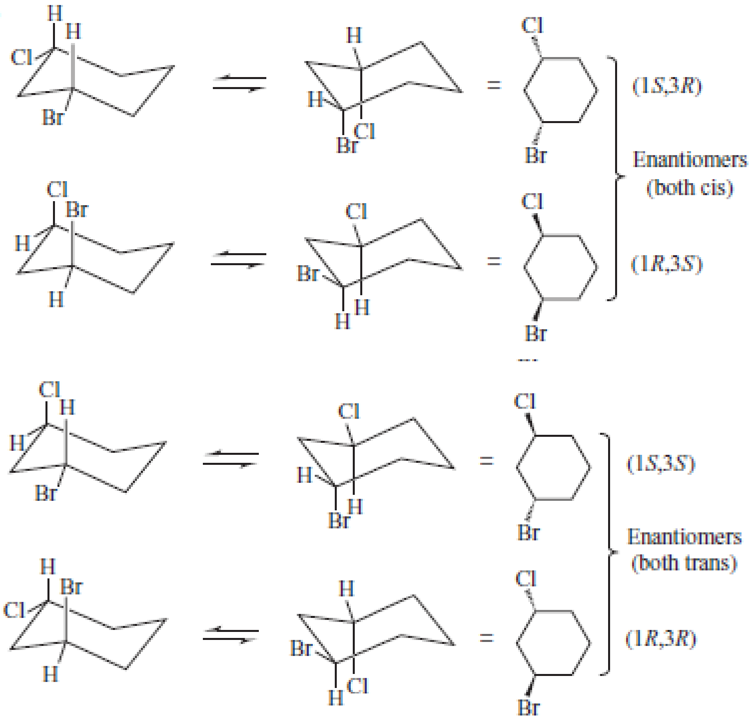
(a)



(b)



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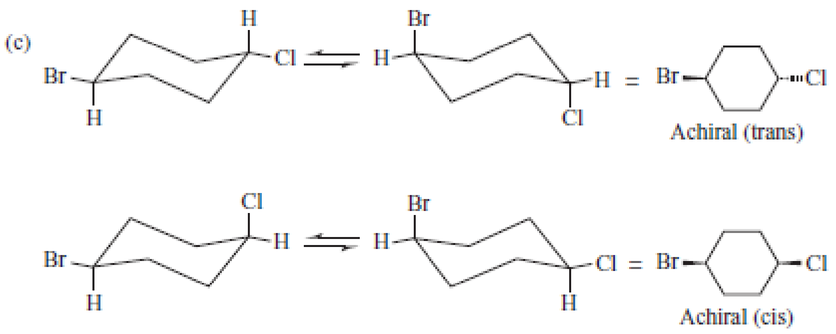
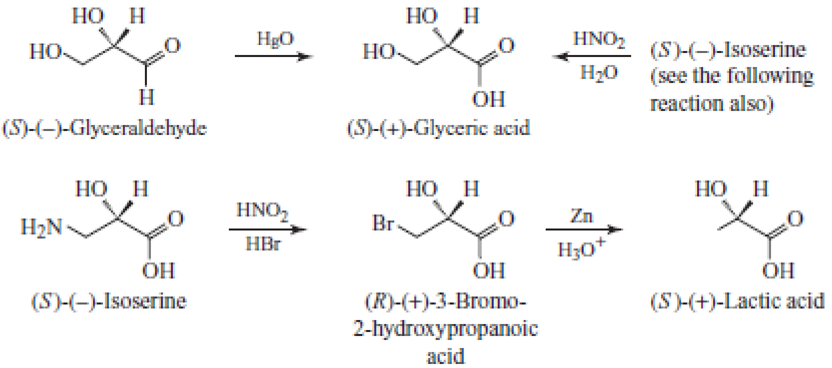


4.26



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Review Problems

Chirality and Stereoisomerism

4.27

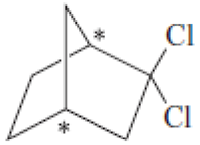
(a), (b), (f), and (g) only

4.28

(a) Seven.

(b) (*R*)- and (*S*)-3-Methylhexane and (*R*)- and (*S*)-2,3-dimethylpentane.

4.29

(a) 

(b) Two, indicated by asterisks in (a)

(c) Four

(d) Because a trans arrangement of the one carbon bridge is structurally impossible. Such a molecule would have too much strain.

4.30

(a) **A** is (2*R*,3*S*)-2,3-dichlorobutane; **B** is (2*S*,3*S*)-2,3-dichlorobutane; **C** is (2*R*,3*R*)-2,3-dichlorobutane.

(b) **A**

4.31

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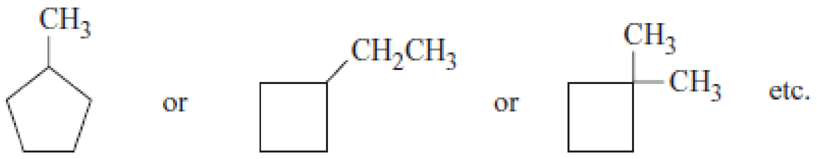
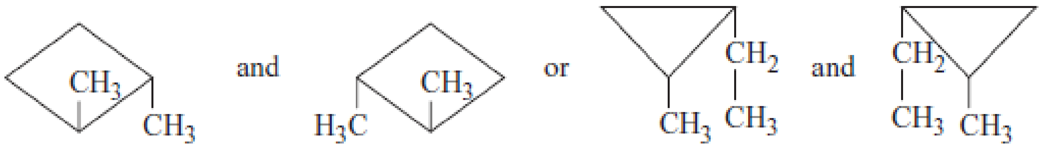
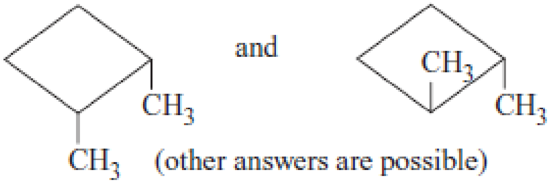
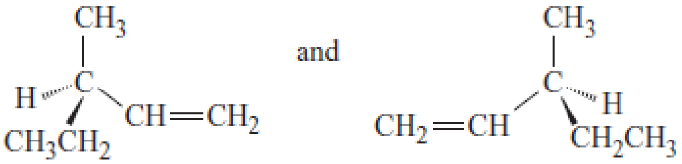
(a) 

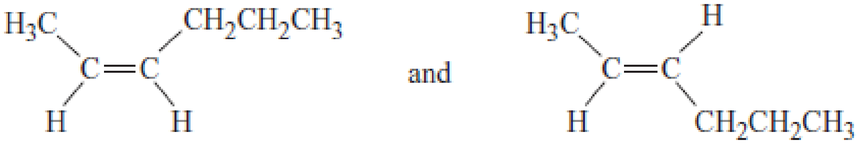
(b) 

(other answers are possible)

(c) 

(other answers are possible)

(d) 

(e) 

(other answers are possible)

4.32

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(a) Same: (S)

(b) Enantiomers: left (S); right (R)

(c) Diastereomers: left (1S, 2S); right (1R, 2S)

(d) Same: (1S, 2S)

(e) Diastereomers: left (1S, 2S); right (1S, 2R)

(f) Constitutional isomers: both achiral

(g) Diastereomers: left, cis (4S); right, trans (4R)

(h) Enantiomers: left (1S, 3S); right (1R, 3R)

(i) Same: no chirality centers

4.33

All of these molecules are expected to be planar. Their stereochemistry is identical to that of the corresponding chloroethenes. (a) can exist as cis and trans isomers. Only one compound exists in the case of (b) and (c).

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4.34

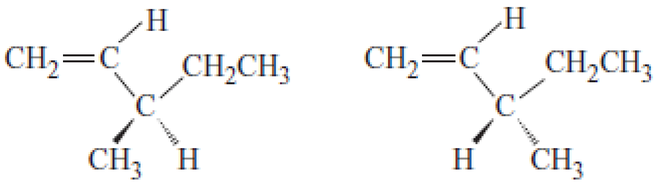
(a) diastereomers

(b) enantiomers

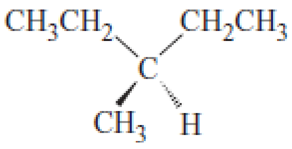
(c) enantiomers

(d) same compound

4.35

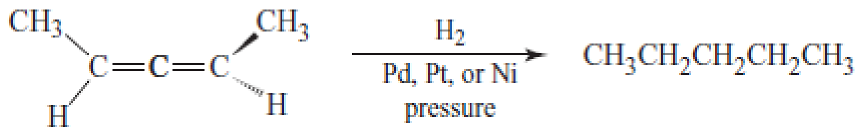


D (racemic)



E (achiral)

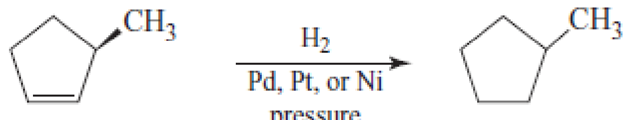
4.36



(or enantiomer)
F

(achiral)
G

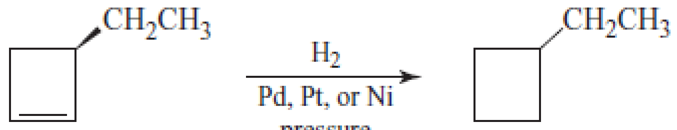
4.37



(or enantiomer)
H

(achiral)
I

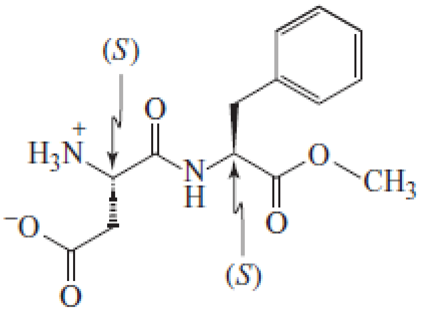
or



(or enantiomer)

(achiral)

4.38



Aspartame

4.39

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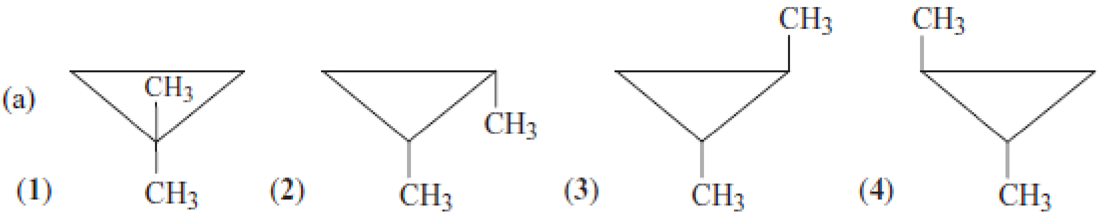
(a)



(b) (3) and (4) are chiral and are enantiomers of each other.

(c) Three fractions: a fraction containing (1), a fraction containing (2), and a fraction containing (3) and (4) [because, being enantiomers, (3) and (4) would have the same vapor pressure].

(d) None

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

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1. (d) Both are identical.

2. (d) The two isomers would have the Cl atom at 1 and 2 positions respectively.

3. (d) All alpha H would be replaced with D.

4. (d) In the mechanism, alpha H is replaced as a proton by the base.

5. (b) One isomer is meso while two are optically active.

6. (c) Due to formation of stable aromatic enol form.

7. (d) It is an alkene with C=C. Two Geometrical Isomers would be possible for each combination of two halogens on each side of the double bond.

8. (c) Both the molecules have R configuration.

9. Correction!!! 2 and 3 numbering of C atoms should be interchanged. Conformer obtained would be gauche as both the methyl groups would be at 60° to each other.

10. (c) Enantiomers are stereoisomers that are mirror images of each other.

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11. (b) Chiral compounds are those that lack symmetry and are optically active. 1-chloro-2-methylbutane and 2-chloro-3-methylbutane are the optically active products and both exist in 2 enantiomeric forms.

12. (d) It has a plane of symmetry which passes diagonally cutting across the Cl and Br atoms.

13.(c) The five isomers are : hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane.

14. (b) Separation of enantiomers is known as resolution.

15. (a) It has a plane of symmetry which passes diagonally cutting across the two trans methyl groups.

16. (d) The meso isomer would have both the Cl atoms on the same side in fischer projection.

17. (b) First molecule is aromatic in both the given keto form as well as its enol form, thus no major driving force towards enol, while in molecule B, the molecule converts from non-aromatic to aromatic in its enol form, thus greater enol content.

18. (b) It is meso as it has a plane of symmetry.

19. (c) One in the molecular plane (xy plane) and two in the x-z and y-z planes cutting the molecule symmetrically.

20. (b) The molecules 1 and 4 are GI of the given molecule.

21. (b) The molecular plane.

22. (c) It has no symmetry as the valencies on the two terminals of the even cumulene are perpendicular.

23. (c) The three alpha H would be replaced by D.

24. (b) Centre of symmetry means line joining like groups must pass through the centre of molecule.

25. (b) This is α hydroxyl keto-enol tautomerism.

26. (d) Both would not undergo tautomerism as the enol would violate Bredt's rule. Bridge-head H atoms do not participate in Tautomerism.

27. (b) Apply CIP (Cahn-Ingold-Prelog) rules to assign priority and determine R or S.

28. (b) Both the rings would go out of plane due to steric repulsion between the two methyl groups. The molecule would thus not have any symmetry.

29. (b) The second molecule is meso due to plane of symmetry, thus it does not exhibit optical activity.

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30. (c) Two systems show stereoisomerism here, the pi bond and the chiral carbon. Thus total stereoisomers = $2^2 = 4$.

31. (c) (d) Both c and d do not have any symmetry, thus they are chiral. While a and b both have a plane of symmetry in the molecular plane.

<H2> Multiple Correct Choice Type

1. (a) (d) The compound is optically active as it doesn't possess centre of symmetry or plane of symmetry. The molecule possesses a C_2 axis of symmetry (i.e. it can be rotated by 180° and the product obtained is same.)

<H2> Integer Type

1. (3) The three alkynes are pent-1-yne, pent-2-yne and 3-methylbut-1-yne.

2. (3) The three possible relative positions of the three methyl groups on benzene would be (1,2,3), (1,2,4), and (1,3,5).

3. (4) Enol would be formed on the left side as well as the right side of the keto carbon. Both would have 2 geometrical isomers (E and Z forms).

4. (4) The four stereoisomers are: when all three groups Cl,Cl and OH are on same side (above or below) of ring (optically inactive); when OH and one Cl are on same side and the other Cl on opposite side (optically active so two isomers); when both Cl are on same side and the OH group is on the opposite side (optically inactive).

5. (2) The meso forms are when all the three Cl atoms are on same side of ring and when the top Cl atom is on opposite side while the bottom two Cl atoms are on the same side. Both these molecules would have a plane of symmetry. Meso compound means a compound has both a chiral carbon as well as symmetry.

<H2> Matrix Match Type

1. $\mathbf{a \rightarrow (p, q); b \rightarrow (p, q); c \rightarrow (p, q); d \rightarrow (p, r)}$

In (a), (b) and (c) both cis and trans (with respect to methyl and ethyl) are possible and the trans form is optically active. In (d), two GI are possible: when all three methyl are on same side and one where one of the methyl is on opposite side, but both have a plane of symmetry thus they are optically inactive.

2. $a \rightarrow (p); b \rightarrow (q); c \rightarrow (r); d \rightarrow (s)$

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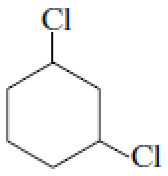
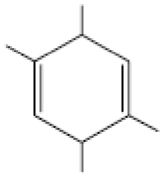
In A, the two isomers are n-butane and iso-butane.

In B, the two isomers are n-pentane (C-C-C-C-C), iso-pentane (C-C(CH_3)-C-C) and neo-pentane (C(CH_3)$_4$).

In C, the five isomers are n-hexane; 2-methylpentane; 3-methylpentane; 2,2-dimethylbutane and 2,3-dimethylbutane.

In D, the nine isomers are: (C-C-C-C-C-C-C); (C-C(C)-C-C-C-C); (C-C-C(C)-C-C-C); (C-C(C)$_2$-C-C-C); (C-C(C)-C(C)-C-C); (C-C(C)-C-C(C)-C); (C-C-C(C)$_2$-C-C); (C-C-C(C-C)-C-C); (C-C(C)$_2$-C(C)-C).

3.

Column I	Column II
(a) 2,3–Dihydroxybutane–1,4–dioic acid.	(p) Number of meso stereoisomer is odd.
(b) 2,3,4–Trichloropentane	(q) Number of meso stereoisomer is even.
(c) 	(r) Number of optically active isomer is even.
(d) 	(s) Number of optically active isomer is odd.
	(t) Total number of stereoisomer is odd.

Solution

$a \rightarrow (p, r, t); b \rightarrow (q, r); c \rightarrow (p, r, t); d \rightarrow (p, r, t)$

A has one meso and two optically active. B has two meso and two optically active. C has one meso (cis) and two optically active (trans). D has one meso (trans has centre of symmetry) and two optically active (cis).

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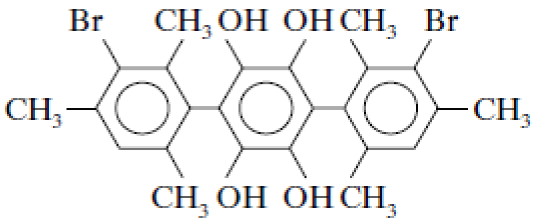
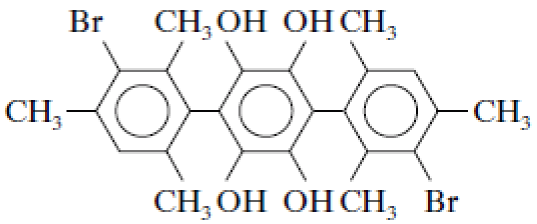
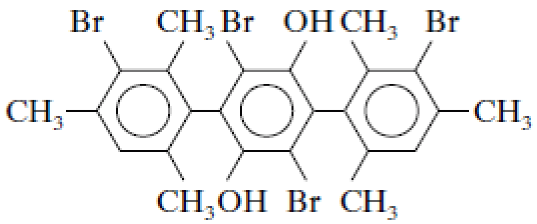
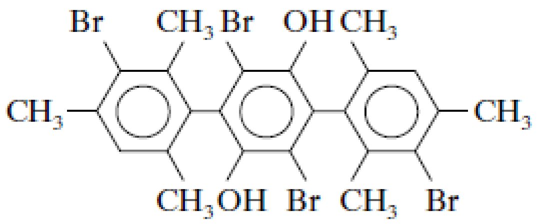
4.

Column I	Column II
(a) 	(p) C_2 (Axis of symmetry)
(b) 	(q) POS (Plane of symmetry)
(c) 	(r) COS (Center of symmetry)
(d) 	(s) Optically inactive

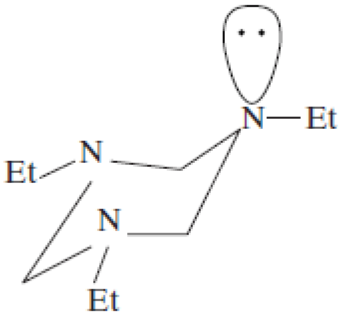
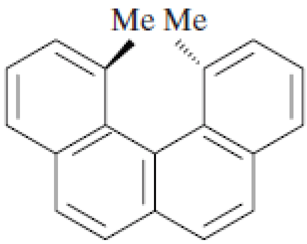
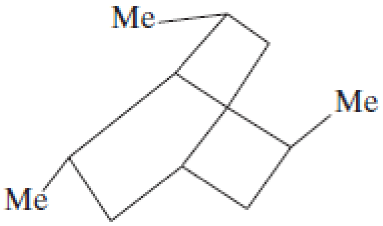
Solution

a → (p, q, s); b → (p, q, r, s); c → (p); d → (r, s)

C_2 implies that upon rotation by 180°, we get identical product. Plane of symmetry cuts the molecule into two halves that are mirror images of each other. Centre of symmetry means that line joining like groups passes through the centre of the molecule.

Solution Manual for Solomons, Fryhle and Snyder Organic Chemistry For JEE (Main & Advanced), Copyright©2017 Wiley India Pvt. Ltd. All rights reserved

5.

Column I	Column II
(a) 	**(p)** COS (Center of symmetry)
(b) 	**(q)** POS (Plane of symmetry)
(c) 	**(r)** AOS (Axis of symmetry)
(d) 2,2,3,3-Tetramethly butane in staggered state	**(s)** Optically active

Solution

a → (q, r); b → (r, s); c → (r, s); d → (p, q, r)

A has POS cutting across the middle of the chair form and has C_3 axis of symmetry. B has C_2 axis of symmetry. C has C_3 axis of symmetry. D has POS, COS, (C_2 and C_3).

Chapter 5: Nomenclature and Conformations of Alkanes and Cycloalkanes

Practice Problems

5.1

or

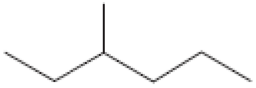
$CH_3(CH_2)_5CH_3$

Heptane

or

$(CH_3)_2CHCH_2CH_2CH_2CH_3$

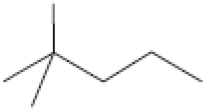
2-Methylhexane



or

$I_3CH_2CH(CH_3)CH_2CH_2CH_3$

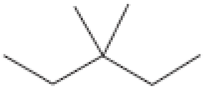
3-Methylhexane



or

$(CH_3)_3CCH_2CH_2CH_3$

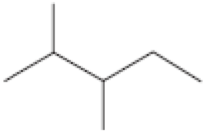
2,2-Dimethylpentane



or

$(CH_3CH_2)_2C(CH_3)_2$

3,3-Dimethylpentane



or

$(CH_3)_2CHCH(CH_3)CH_2CH_3$

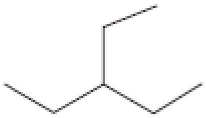
2,3-Dimethylpentane

EY

or

$(CH_3)_2CHCH_2CH(CH_3)_2$

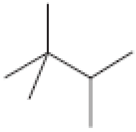
2,4-Dimethylpentane



or

$(CH_3CH_2)_3CH$

3-Ethylpentane



or

$(CH_3)_3CCH(CH_3)_2$

2,2,3-Trimethylbutane

5.2

(d); it represents 3-methylpentane

5.3

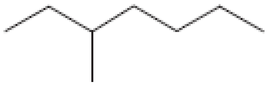
$CH_3CH_2CH_2CH_2CH_2CH_3$ hexane

5.4

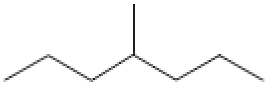
WILEY

(a,b)

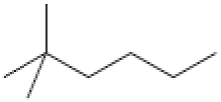
2-Methylheptane



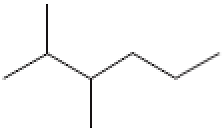
3-Methylheptane



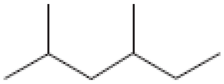
4-Methylheptane



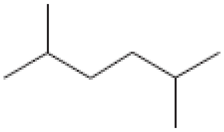
2,2-Dimethylhexane



2,3-Dimethylhexane

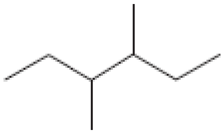


2,4-Dimethylhexane

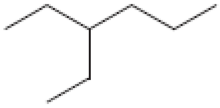


2,5-Dimethylhexane

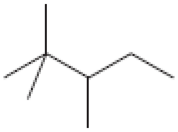
3,3-Dimethylhexane



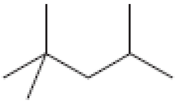
3,4-Dimethylhexane



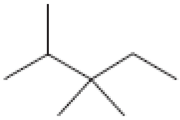
3-Ethylhexane



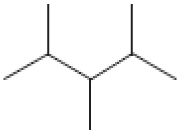
2,2,3-Trimethylpentane



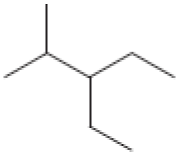
2,2,4-Trimethylpentane



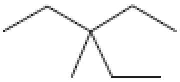
2,3,3-Trimethylpentane



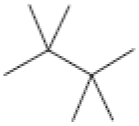
2,3,4-Trimethylpentane



3-Ethyl-2-methylpentane



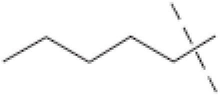
3-Ethyl-3-methylpentane



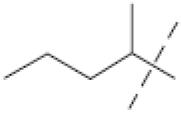
2,2,3,3-Tetramethylbutane

5.5

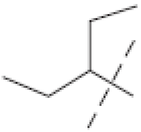
(a)



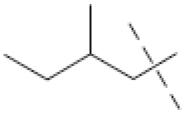
Pentyl



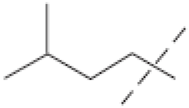
1-Methylbutyl



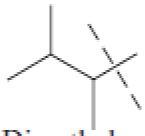
1-Ethylpropyl



2-Methylbutyl



3-Methylbutyl



1,2-Dimethylpropyl

1,1-Dimethylpropyl

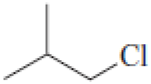
(b) See the answer to Review Problem 4.1 for the formulas and names of C_7H_{16} isomers.

5.6

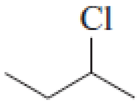
WILEY

(a)

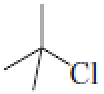
1-Chlorobutane



1-Chloro-2-methylpropane



2-Chlorobutane

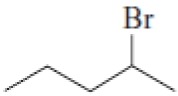


2-Chloro-2-methylpropane

(b)

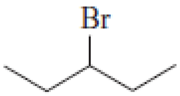
1-Bromopentane

1-Bromo-3-methylbutane

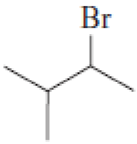


2-Bromopentane

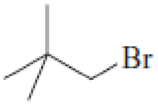
1-Bromo-2-methylbutane



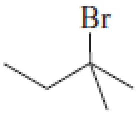
3-Bromopentane



2-Bromo-3-methylbutane



1-Bromo-2,2-dimethylpropane

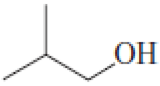


2-Bromo-2-methylbutane

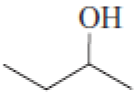
5.7

(a)

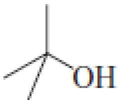
1-Butanol



2-Methyl-1-propanol



2-Butanol

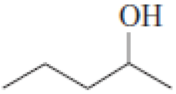


2-Methyl-2-propanol

(b)

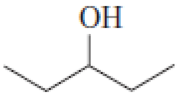
1-Pentanol

3-Methyl-1-butanol

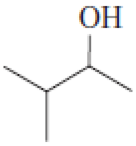


2-Pentanol

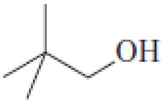
2-Methyl-1-butanol



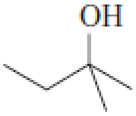
3-Pentanol



3-Methyl-2-butanol



2,2-Dimethyl-1-propanol



2-Methyl-2-butanol

5.8

(a) 1,1-Dimethylethylcyclopentane or *tert*-butylcyclopentane

(b) 1-Methyl-2-(2-methylpropyl)cyclohexane or 1-isobutyl-2-methylcyclohexane

(c) Butylcyclohexane

(d) 1-Chloro-2,4-dimethylcyclohexane

(e) 2-Chlorocyclopentanol

(f) 3-(1,1-Dimethylethyl)cyclohexanol or 3-*tert*-butylcyclohexanol

5.9

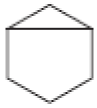
(a) 2-Chlorobicyclo[1.1.0]butane

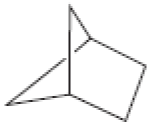
(b) Bicyclo[3.2.1]octane

(c) Bicyclo[2.1.1]hexane

(d) 9-Chlorobicyclo[3.3.1]nonane

(e) 2-Methylbicyclo[2.2.2]octane

(f)  Bicyclo[3.1.0]hexane or

 bicyclo[2.1.1]hexane

5.10

(a) *trans*-3-Heptene

(b) 2,5-Dimethyl-2-octene

(c) 4-Ethyl-2-methyl-l-hexene

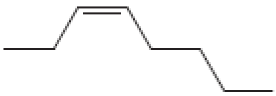
(d) 3,5-Dimethylcyclohexene

(e) 4-Methyl-4-penten-2-ol

(f) 2-Chloro-3-methylcyclohex-3-en-1-ol

5.11

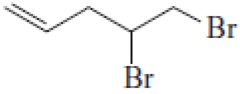
WILEY

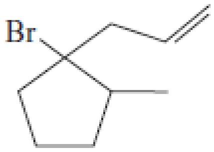
(a) 

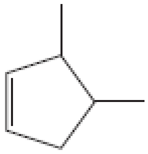
(b)

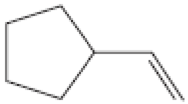
(c)

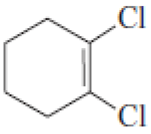
(d)

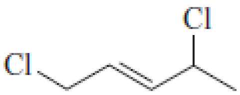
(e) 

(f) 

(g) 

(h) 

(i) 

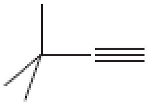
(j) 

5.12

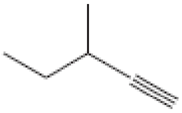
1-Hexyne

2-Hexyne

3-Hexyne

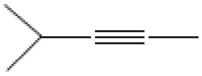


3,3-Dimethyl-1-butyne



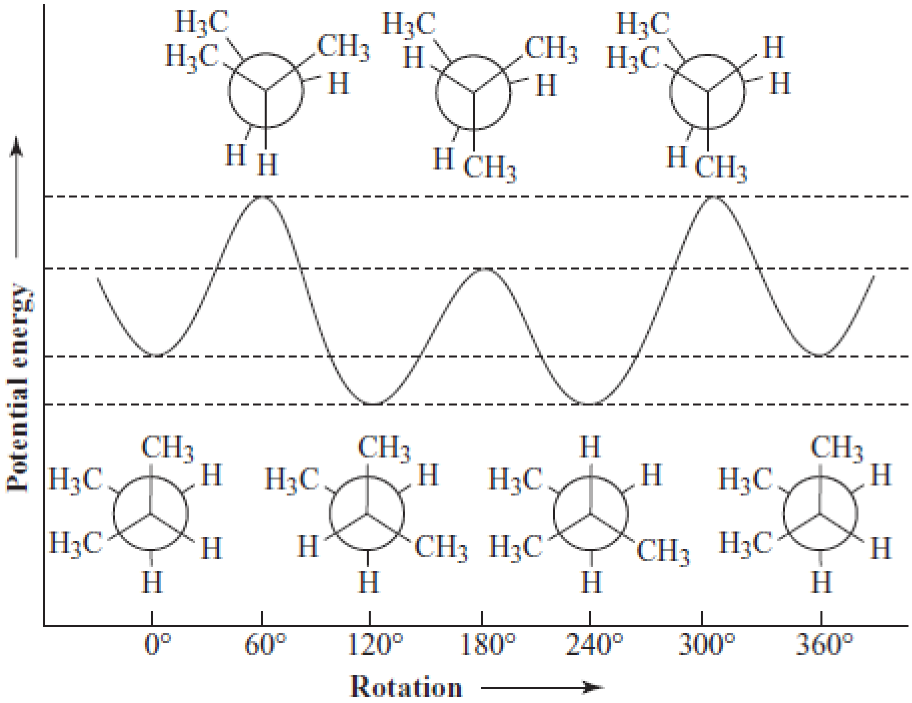
3-Methyl-1-pentyne

4-Methyl-1-pentyne



4-Methyl-2-pentyne

5.13



5.14

$$\log K_{eq} = \frac{\Delta G^\circ}{-2.303RT} = \frac{-7600\ \text{J}}{(-2.303)(8.314\ \text{J K}^{-1})(298\ \text{K})} = 1.32$$

$K_{eq} = 21.38$

Let e = amount of equatorial form

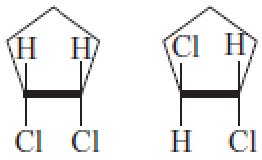
and a = amount of axial form

then, $K_{eq} = \dfrac{e}{a} = 21.38$

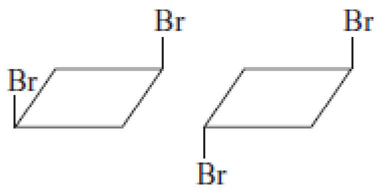
$e = 21.38a$

$$\% e = \frac{21.38a}{a + 21.38a} \times 100 = 95.5\%$$

5.15

(a) 

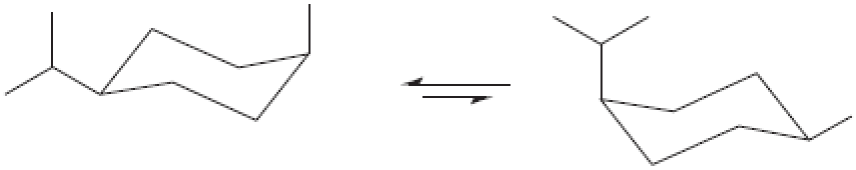
(cis) (trans)

(b) 

(cis) (trans)

(c) No

5.16

(a-d) 

More stable because larger group is equatorial and so preferred at equilibrium

Less stable because larger group is axial

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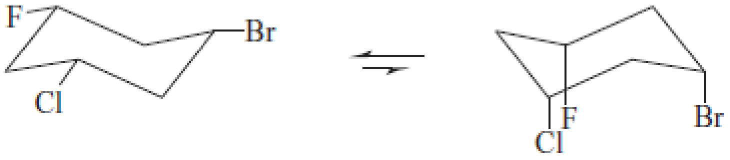
5.17

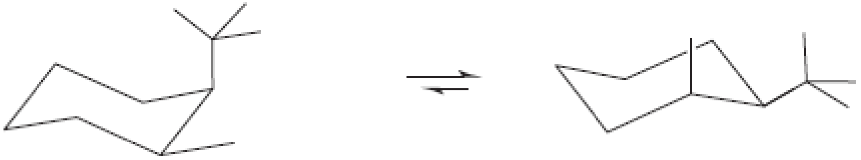


all equatorial (more stable)

all axial (less stable)

5.18

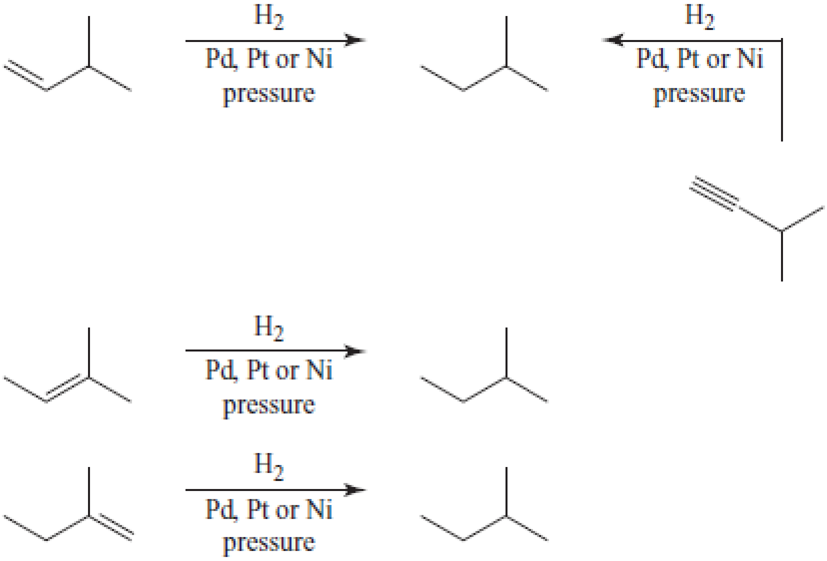
(a,b)



Less stable because the large *tert*-butyl group is axial (more potential energy)

More stable because the large *tert*-butyl group is equatorial (less potential energy)

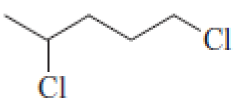
5.19

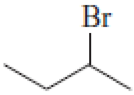


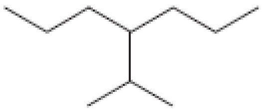
REVIEW PROBLEMS

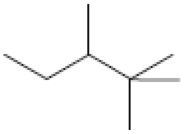
Nomenclature and Isomerism

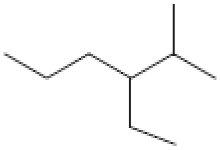
5.20

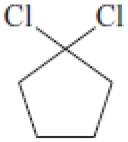
(a) 

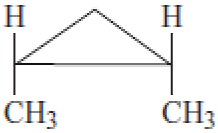
(b) 

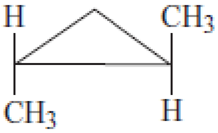
(c) 

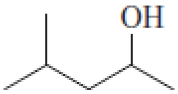
(d) 

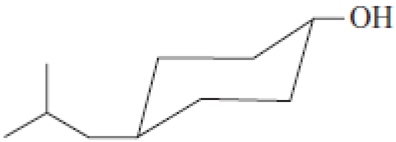
(e) 

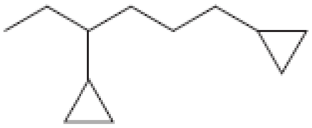
(f) 

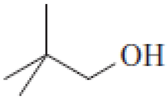
(g) 

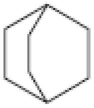
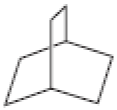
(h) 

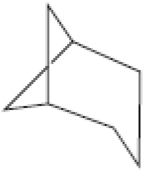
(i) 

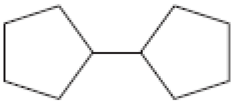
(j) 

(k) 

(l) 

(m)  or 

(n) 

(o) 

5.21

(a) 5-Ethyl-7-isopropyl-2,3-dimethyldecane

(b) 2,2,5-Trimethylhexane

(c) 4-Bromo-6-chloro-3-methyloctane

(d) 2-Methyl-1-butanol

(e) 2-Bromobicyclo[3.3.1]nonane

(f) *trans*-1-Bromo-3-fluorocyclopentane

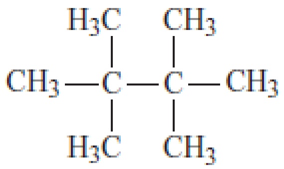
(g) 5,6-Dimethyl-2-heptane

(h) 7-Chlorobicyclo[2.2.1]heptane

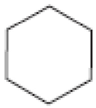
5.22

The two secondary carbon atoms in *sec*-butyl alcohol are equivalent; however, there are three five-carbon alcohols (pentyl alcohols) that contain a secondary carbon atom.

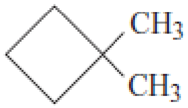
5.23

(a) 

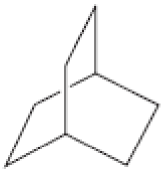
2,2,3,3-Tetramethylbutane

(b) 

Cyclohexane

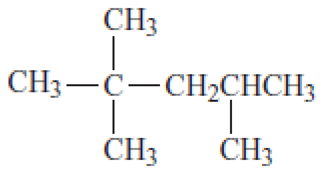
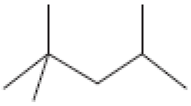
(c) 

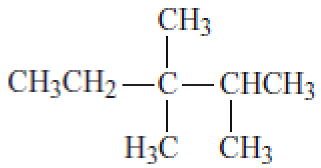
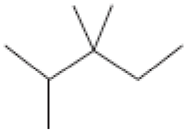
1,1-Dimethylcyclobutane

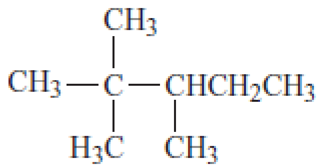
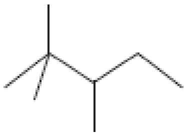
(d) 

Bicyclo[2.2.2]octane

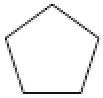
5.24

 or  2,2,4-trimethylpentane

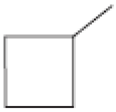
 or  2,3,3-trimethylpentane

 or  2,2,3-trimethylpentane

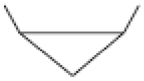
5.25



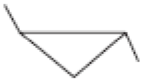
Cyclopentane



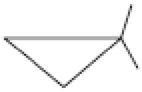
Methylcyclobutane



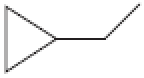
cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane



1,1-Dimethylcyclopropane



Ethylcyclopropane

5.26

$S - A + 1 = N$

For cubane, $S = 12$ and $A = 8$. Thus $12 - 8 + 1 = N$; $N = 5$ rings in cubane.

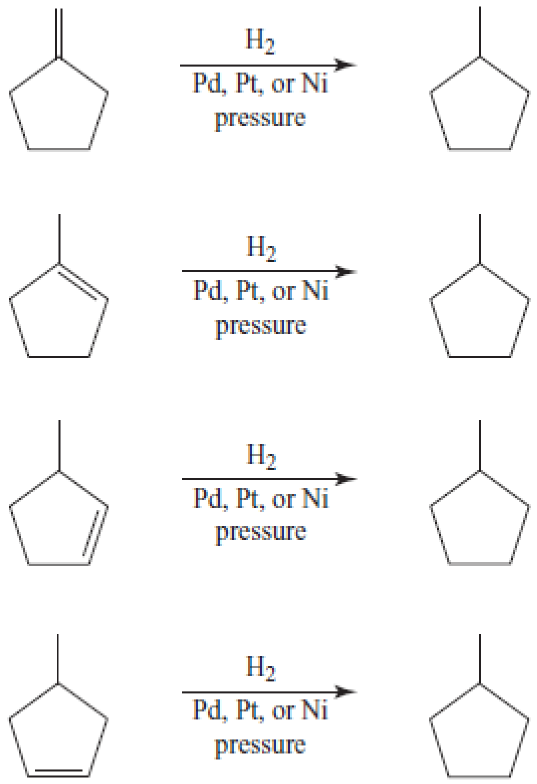
5.27

A homologous series is one in which each member of the series differs from the one preceding it by a constant amount, usually a CH_2 group. A homologous series of alkyl halides would be the following:

CH_3X
CH_3CH_2X
$CH_3(CH_2)_2X$
$CH_3(CH_2)_3X$
$CH_3(CH_2)_4X$
etc.

Hydrogenation

5.28



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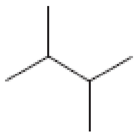
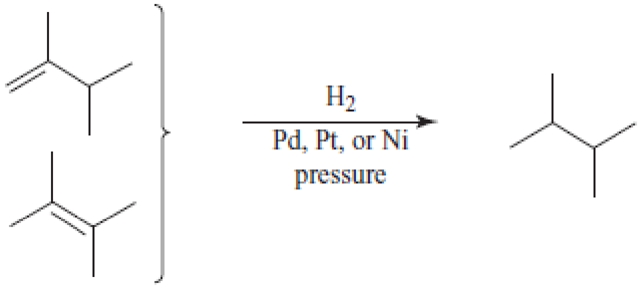
5.29



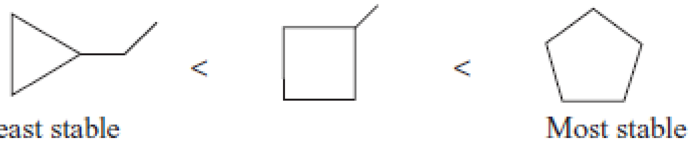
2,3-Dimethylbutane

From two alkenes



Conformations and Stability

5.30



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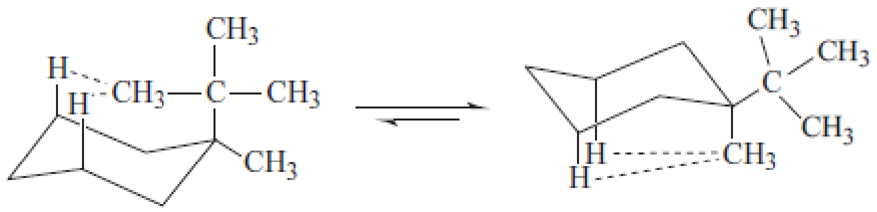
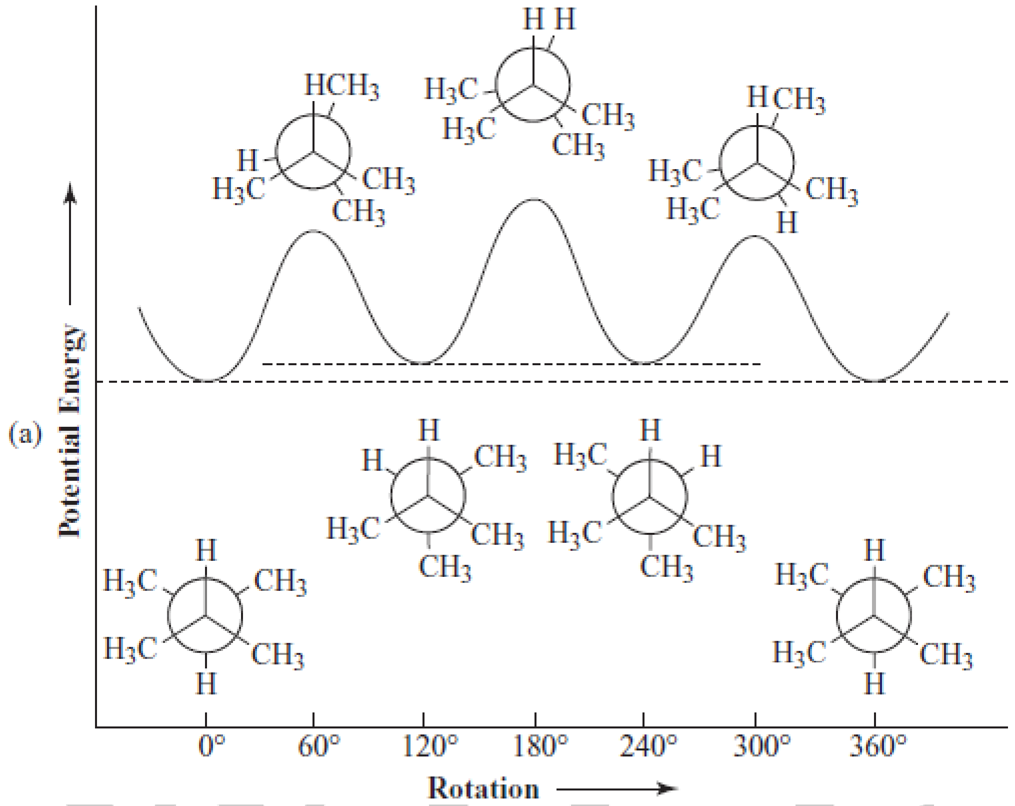
5.31

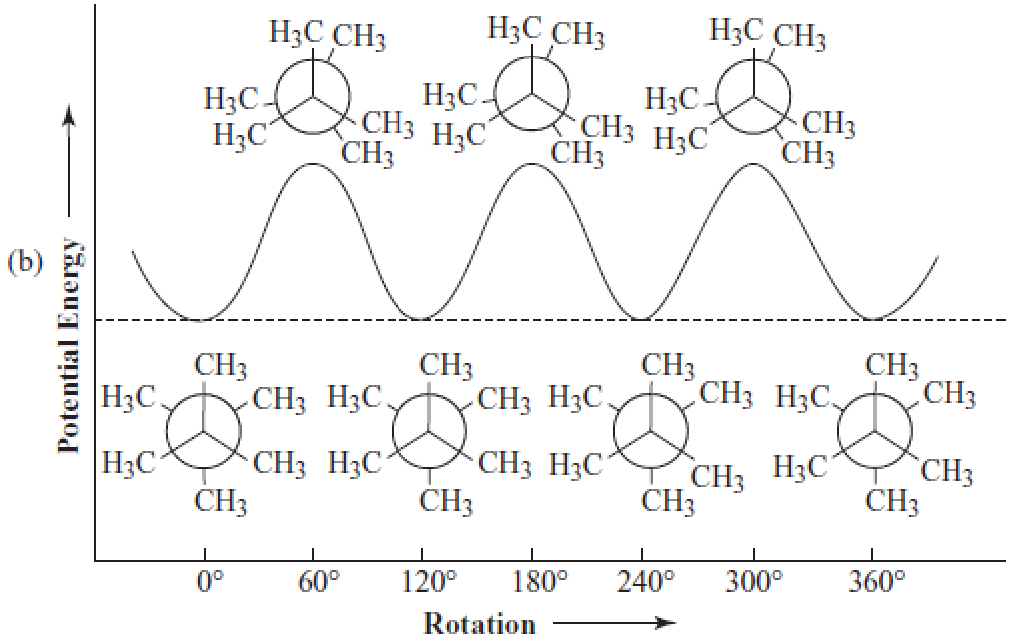


This conformation is *less stable* because 1,3-diaxial interactions with the large *tert*-butyl group cause considerable repulsion.

This conformation is *more stable* because 1,3-diaxial interactions with the smaller methyl group are less repulsive.

5.32


(a)
Potential Energy
Rotation
0°
60°
120°
180°
240°
300°
360°


(b)
Potential Energy
Rotation
0°
60°
120°
180°
240°
300°
360°

5.33

(a) Pentane would boil higher because its chain is unbranched. Chain-branching lowers the boiling point.

(b) Heptane would boil higher because it has the larger molecular weight and would, because of its larger surface area, have larger van der Waals attractions.

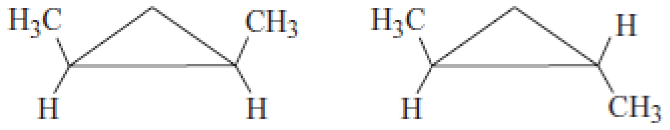
(c) 2-Chloropropane because it is more polar and because it has a larger molecular weight.

(d) 1-Propanol would boil higher because its molecules would be associated with each other through hydrogen-bond formation.

(e) Propanone (CH_3COCH_3) would boil higher because its molecules are more polar.

5.34

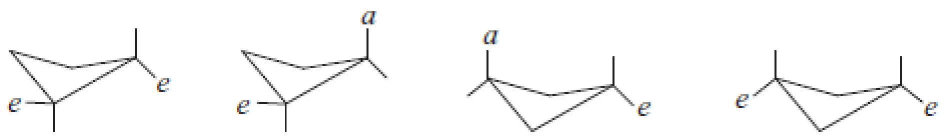
trans-1,2-Dimethylcyclopropane would be more stable because there is less crowding between its methyl groups.



Less stable   More stable

5.35

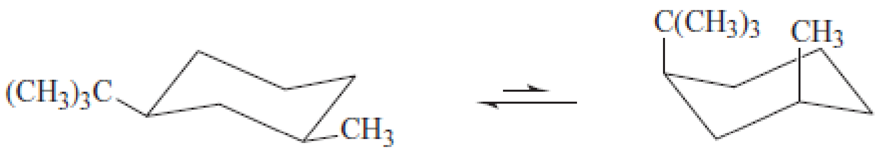
For 1,2-disubstituted cyclobutanes, the trans isomer is *e*,*e*; the cis isomer is *a*,*e*, and so the less stable of the two. For 1,3-disubstituted cyclobutanes, the cis isomer is *e*,*e* and more stable than the *a*,*e* trans isomer.



Trans   Cis   Trans   Cis

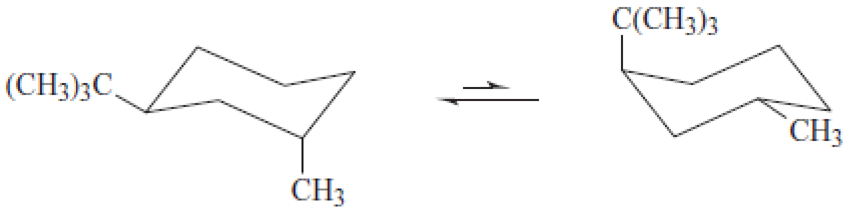
5.36

(a)



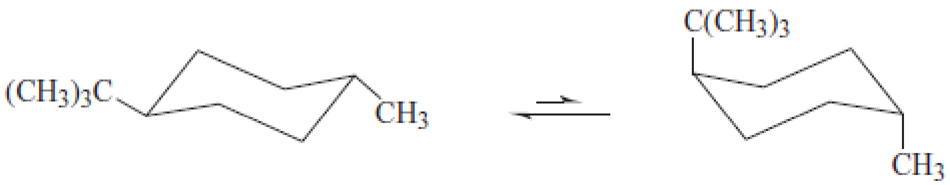
More stable conformation because
both alkyl groups are equatorial

(b)



More stable because larger group
is equatorial

(c)



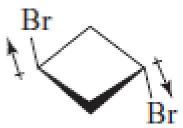
More stable conformation because
both alkyl groups are equatorial

(d)

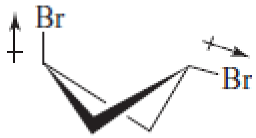
More stable because larger group
is equatorial

5.37

If the cyclobutane ring were planar, the C—Br bond moments would exactly cancel in the trans isomer. The fact that *trans*-1,3-dibromocyclobutane has a dipole moment shows the ring is not planar.



Planar form
$\mu = 0$ D



Bent form
$\mu \neq 0$ D

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (a) In b,c,d the longest chain has not been chosen as the parent chain.

2. **(d)** Longest chain is of 8 members.

3. **(a)** Numbering would start from left as per lowest locant rule.

4. **(d)** Isopropyl group is [$(CH_3)_2CH$-].

5. **(c)** Both gauche and anti lies at energy minima on the graph.

6. **(b)** Numbering would start from the carbon of ring with which the methyl substituent is attached and would then continue along the pi bond.

7. **(c)** It represents the most stable anti-conformer of 1-iodo-2-methylpropane.

8. **(d)**

9. **(b)** Numbering would start from the left as in case of tie between double and triple bond in numbering, double bond is given preference as per IUPAC nomenclature rules.

10. **(c)** Bulky group at equatorial position is more stable and here the tertiary butyl group which is more bulky should preferably at equatorial, Thus reactant would be favored at equilibrium.

11. **(a)** Triheptacontane indicates 73 carbon atoms.

12. **(d)** II has more steric strain than I due to the bulky groups methyl coming close in gauche conformer.

13. **(c)** Numbering starts from the C atom to which the OH group is attached.

14. **(b)** Both the methyl groups are in the axial position.

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15. **(b)** Most stable is gauche due to H bond between the OH group and F.

16. **(a)** Phenol has OH group attached to benzene directly.

17. **(b)** Only one of the two substituents can be at equatorial position as the groups are attached in trans configuration. Hence the more bulky group tert-butyl should be at equatorial.

18. **(a)** As per IUPAC rules for naming of complex substituents.

19. **(c)** On the basis of H bonding between OH and F groups and on the basis of steric factor.

20. **(c)** For isomers, heat of combustion is inversely proportional to stability. C is least stable due to high angle strain in cyclopropyl rings.

21. **(b)** Neopentane is $(CH_3)_4C$.

22. **(c)** More the number of C atoms, more is the heat of combustion.

23. **(c)** As they are geometrical isomers , therefore, cannot be interconverted at room temperature due to pi bond.

24. (c) More the number of C atoms, more is the heat of combustion.

25. (b) Both can be interconverted by rotation about the sigma bond.

<H2> Multiple Correct Choice Type

1. (a) (c) sec-butylalcohol is 2-butanol while neo-pentyl alcohol is 2-methylpropan-1-ol.

<H2> Integer Type

1. (4) Parent chain would be the acyclic part as it contains the main functional group ketone and numbering would be from the right.

<H2> Matrix Match Type

1. (a)$\rightarrow$(r); (b)$\rightarrow$(s) ; (c)$\rightarrow$(p); (d)$\rightarrow$(q)

Naming as per IUPAC rules. In numbering, alkene is given preference over substituents.

2. $a \rightarrow (s); b \rightarrow (p); c \rightarrow (q); d \rightarrow (r)$

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Chapter 6: Ionic Reactions

Practice Problems

6.1

(a) *cis*-1-Bromo-2-methylcyclohexane

(b) *cis*-1-Bromo-3-methylcyclohexane

(c) 2,3,4-Trimethylheptane

6.2

(a) 3° (b) alkenyl (vinylic) (c) 2° (d) aryl (e) 1°

6.3

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(a) $CH_3{-}\ddot{\underset{..}{I}}{:} + CH_3CH_2{-}\ddot{\underset{..}{O}}{:}^- \longrightarrow CH_3{-}\ddot{\underset{..}{O}}{-}CH_2CH_3 + {:}\ddot{\underset{..}{I}}{:}^-$

Substrate (CH₃–I); Nucleophile (CH₃CH₂O⁻); Leaving group (I⁻)

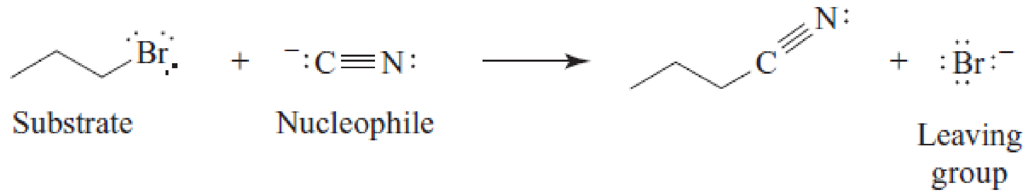
(b) $:\ddot{\underset{..}{I}}:^- + CH_3CH_2{-}\ddot{\underset{..}{Br}}{:} \longrightarrow CH_3CH_2{-}\ddot{\underset{..}{I}}{:} + {:}\ddot{\underset{..}{Br}}{:}^-$

Nucleophile (I^-); Substrate (CH_3CH_2Br); Leaving group (Br^-)

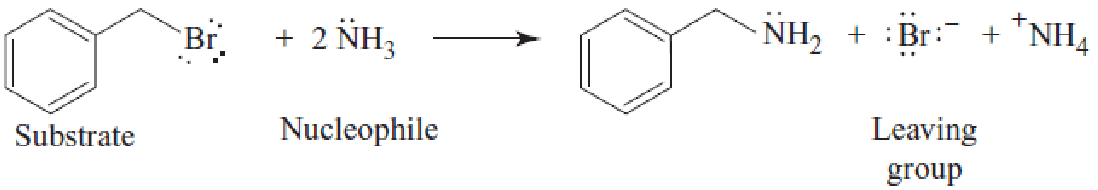
(c) $2\ CH_3\ddot{\underset{..}{O}}H + (CH_3)_3C{-}\ddot{\underset{..}{Cl}}{:} \longrightarrow (CH_3)_3C{-}\ddot{\underset{..}{O}}{-}CH_3 + {:}\ddot{\underset{..}{Cl}}{:}^- + CH_3\overset{+}{\ddot{O}}H_2$

Nucleophile (CH_3OH); Substrate ($(CH_3)_3CCl$); Leaving group (Cl^-)

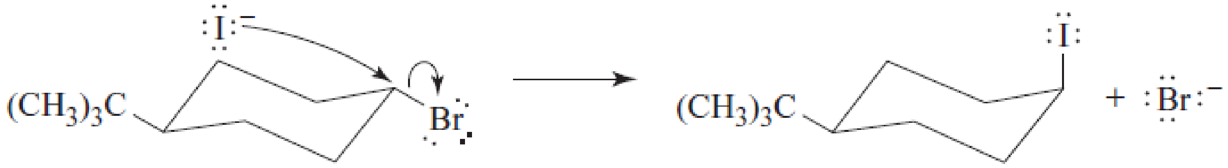
(d)



(e)



6.4



6.5

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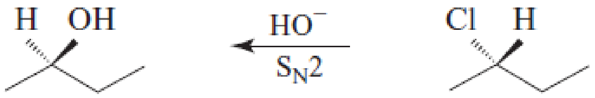
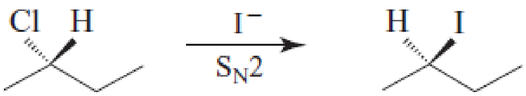
(a) We know that when a secondary alkyl halide reacts with hydroxide ion by substitution, the reaction occurs with *inversion of configuration* because the reaction is S_N2. If we know that the configuration of (−)-2-butanol (from Section 5.8C) is that shown here, then we can conclude that (+)-2-chlorobutane has the opposite configuration.



(*R*)-(−)-2-Butanol $[\alpha]_D^{25°} = -13.52$

(*S*)-(+)-2-Chlorobutane $[\alpha]_D^{25°} = +36.00$

(b) Again the reaction is S_N2. Because we now know the configuration of (+)-2-chlorobutane to be (*S*) [cf., part (a)], we can conclude that the configuration of (−)-2-iodobutane is (*R*).



(*S*)-(+)-2-Chlorobutane (*R*)-(−)-2-Iodobutane

(+)-2-Iodobutane has the (*S*) configuration.

6.6

(b) < (c) < (a) in order of increasing stability

6.7

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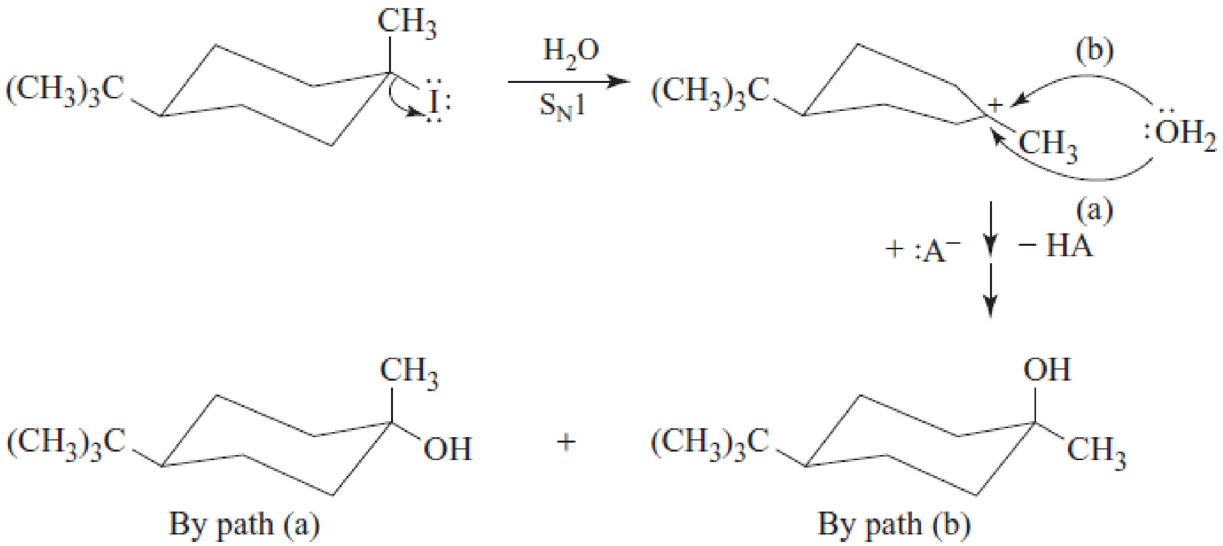
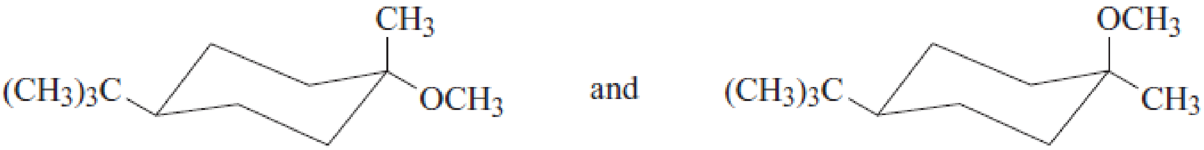
(a, b)



6.8



6.9

(c) is most likely to react by an S_N1 mechanism because it is a tertiary alkyl halide, whereas (a) is primary and (b) is secondary.

6.10

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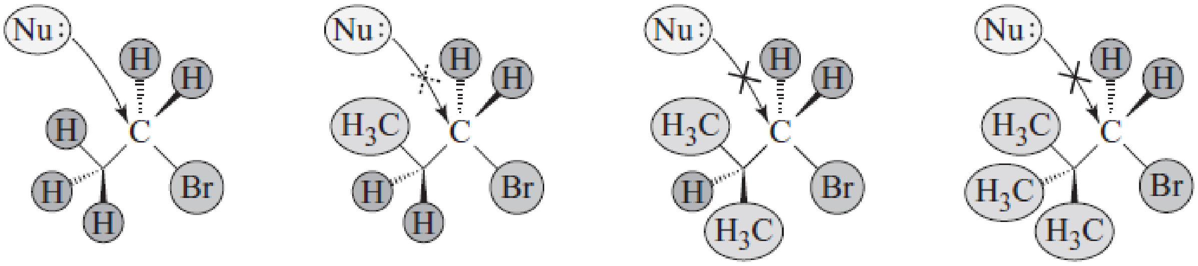
(a) Being primary halides, the reactions are most likely to be S_N2, with the nucleophile in each instance being a molecule of the solvent (i.e., a molecule of ethanol).

(b) Steric hindrance is provided by the substituent or substituents on the carbon β to the carbon bearing the leaving group. With each addition of a methyl group at the β carbon (below), the number of pathways open to the attacking nucleophile becomes fewer.



6.11

$CN^- > CH_3O^- > CH_3CO_2^- > CH_3CO_2H > CH_3OH$

Order of decreasing nucleophilicity in methanol

6.12

$CH_3S^- > CH_3O^- > CH_3CO_2^- > CH_3SH > CH_3OH$

Order of decreasing nucleophilicity in methanol

6.13

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Protic solvents are those that have an H bonded to an oxygen or nitrogen (or to another strongly electronegative atom). Therefore, the protic solvents are formic acid, $H\overset{\overset{O}{\|}}{C}OH$; formamide, $H\overset{\overset{O}{\|}}{C}NH_2$; ammonia, NH_3; and ethylene glycol, $HOCH_2CH_2OH$.
Aprotic solvents lack an H bonded to a strongly electronegative element. Aprotic solvents in this list are acetone, $CH_3\overset{\overset{O}{\|}}{C}CH_3$; acetonitrile, $CH_3C{\equiv}N$; sulfur dioxide, SO_2; and trimethylamine, $N(CH_3)_3$.

6.14

The reaction is an S_N2 reaction. In the polar aprotic solvent (DMF), the nucleophile (CN^-) will be relatively unencumbered by solvent molecules, and, therefore, it will be more reactive than in ethanol. As a result, the reaction will occur faster in *N*,*N*-dimethylformamide.

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6.15

(a) CH_3O^-

(b) H_2S

(c) $(CH_3)_3P$

6.16

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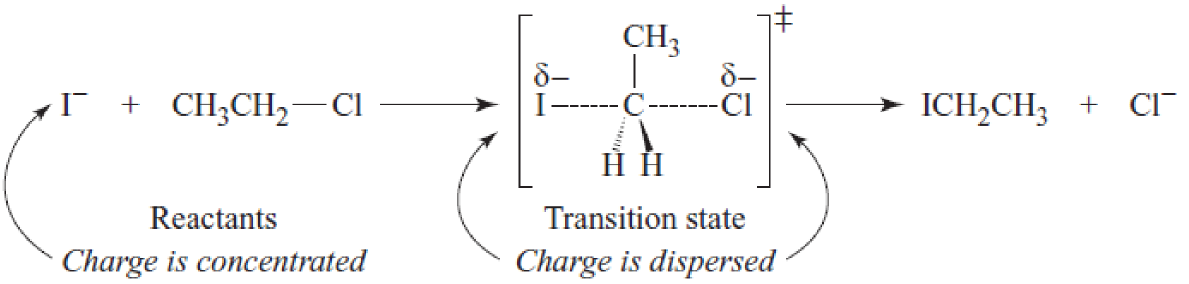
(a) Increasing the percentage of water in the mixture increases the polarity of the solvent. (Water is more polar than methanol.) Increasing the polarity of the solvent increases the rate of the solvolysis because separated charges develop in the transition state. The more polar the solvent, the more the transition state is stabilized (Section 6.13D).

(b) In an S_N2 reaction of this type, the charge becomes dispersed in the transition state:



Increasing the polarity of the solvent increases the stabilization of the reactant I^- more than the stabilization of the transition state, and thereby increases the free energy of activation, thus decreasing the rate of reaction.

WILEY

6.17

$CH_3OSO_2CF_3$ > CH_3I > CH_3Br > CH_3Cl > CH_3F > $^{14}CH_3OH$

(Most reactive) (Least reactive)

6.18

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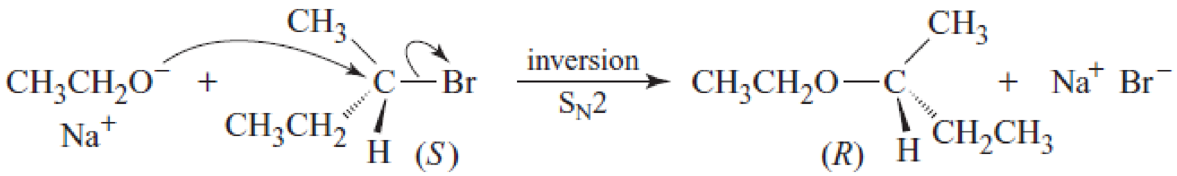
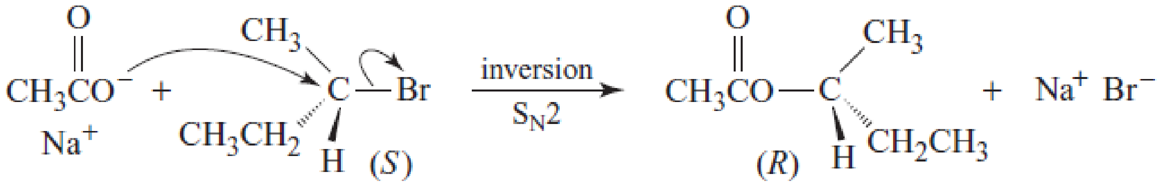
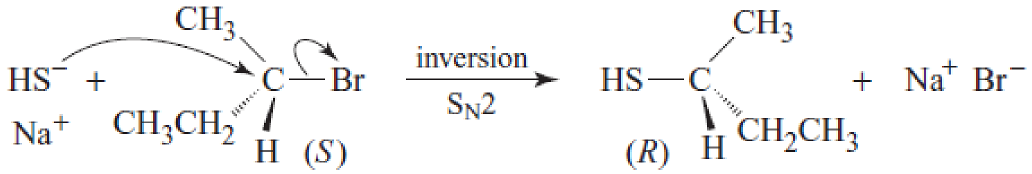
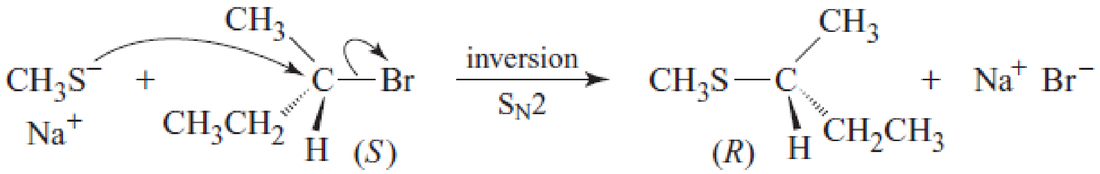
(a) 

(b) 

(c) 

(d) 

Review Problems

Relative Rates of Nucleophilic Substitution

6.19

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(a) 1-Bromopropane would react more rapidly because, being a primary halide, it is less hindered.

(b) 1-Iodobutane, because iodide ion is a better leaving group than chloride ion.

(c) 1-Chlorobutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylpropane.

(d) 1-Chloro-3-methylbutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylbutane.

(e) 1-Chlorohexane because it is a primary halide. Phenyl halides are unreactive in S_N2 reactions.

6.20

(a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol.

(b) Reaction (2) because the ethyl sulfide ion is a stronger nucleophile than the ethoxide ion in a protic solvent. (Because sulfur is larger than oxygen, the ethyl sulfide ion is less solvated and it is more polarizable.)

(c) Reaction (2) because triphenylphosphine $[(C_6H_5)_3P]$ is a stronger nucleophile than triphenylamine. (Phosphorus atoms are larger than nitrogen atoms.)

(d) Reaction (2) because in an S_N2 reaction the rate depends on the concentration of the substrate and the nucleophile. In reaction (2) the concentration of the nucleophile is twice that of the reaction (1).

6.21

(a) Reaction (2) because bromide ion is a better leaving group than chloride ion.

(b) Reaction (1) because water is a more polar solvent than methanol, and S_N1 reactions take place faster in more polar solvents.

(c) Reaction (2) because the concentration of the substrate is twice that of reaction (1). The major reaction would be E2. (However, the problem asks us to consider that small portion of the overall reaction that proceeds by an S_N1 pathway.)

(d) Considering only S_N1 reactions, as the problem specifies, both reactions would take place at the same rate because S_N1 reactions are independent of the concentration of the nucleophile. The predominant process in this pair of reactions would be E2, however.

(e) Reaction (1) because the substrate is a tertiary halide. Phenyl halides are unreactive in S_N1 reactions.

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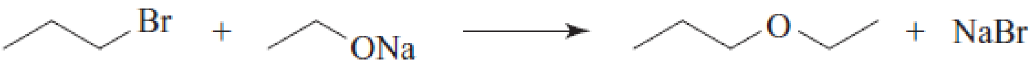
Synthesis

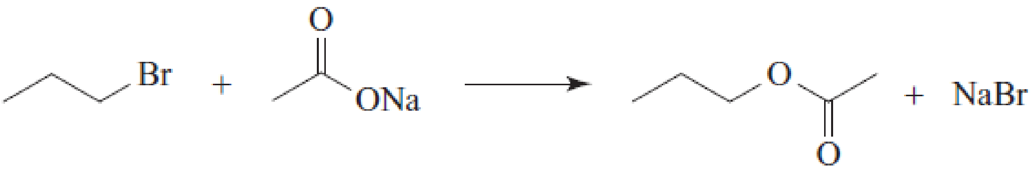
6.22

(a)

(b)

(c) 

(d)

(e) 

(f)

(g)

(h)

(i)

6.23

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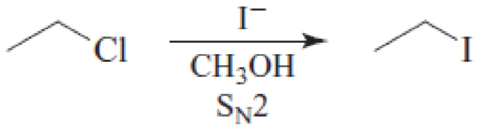
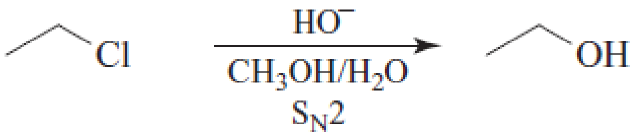
Possible methods are given here.

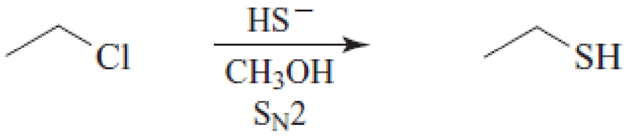
(a) $CH_3Cl \xrightarrow[\substack{CH_3OH \\ S_N2}]{I^-} CH_3I$

(b) 

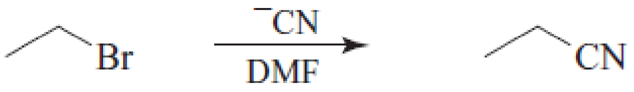
(c) $CH_3Cl \xrightarrow[\substack{CH_3OH/H_2O \\ S_N2}]{HO^-} CH_3OH$

(d) 

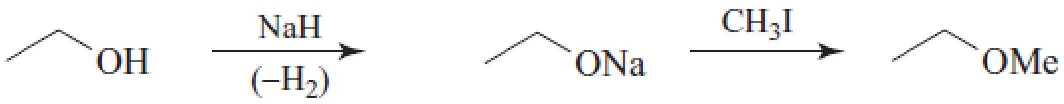
(e) $CH_3Cl \xrightarrow[\substack{CH_3OH \\ S_N2}]{HS^-} CH_3SH$

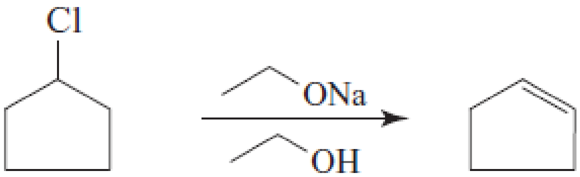
(f) 

(g) $CH_3I \xrightarrow[DMF]{^-CN} CH_3CN$

(h) 

(i) $CH_3OH \xrightarrow[(-H_2)]{NaH} CH_3ONa \xrightarrow[CH_3OH]{CH_3I} CH_3OCH_3$

(j) 

(k) 

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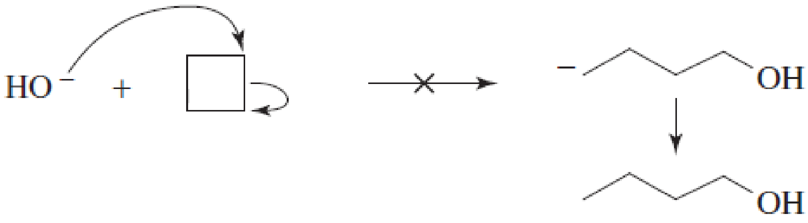
6.24

(a) The reaction will not take place because the leaving group would have to be a methyl anion, a very powerful base, and a very poor leaving group.

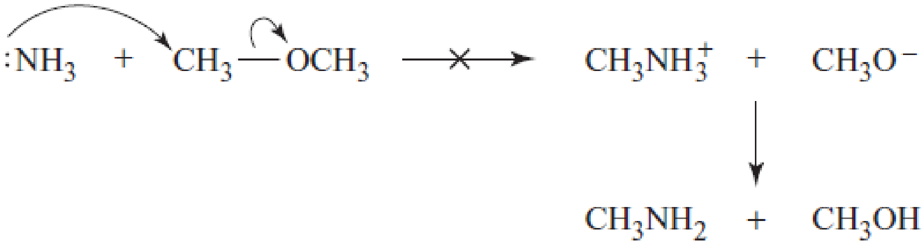
(b) The reaction will not take place because the leaving group would have to be a hydride ion, a very powerful base, and a very poor leaving group.

(c) The reaction will not take place because the leaving group would have to be a carbanion, a very powerful base, and a very poor leaving group.



(d) The reaction will not take place by an S_N2 mechanism because the substrate is a tertiary halide, and is, therefore, not susceptible to S_N2 attack because of the steric hindrance. (A very small amount of S_N1 reaction may take place, but the main reaction will be E2 to produce an alkene.)

(e) The reaction will not take place because the leaving group would have to be a CH_3O^- ion, a strong base, and a very poor leaving group.



(f) The reaction will not take place because the first reaction that would take place would be an acid-base reaction that would convert the ammonia to an ammonium ion. An ammonium ion, because it lacks an electron pair, is not nucleophilic.

$$NH_3 + CH_3\overset{+}{O}H_2 \rightleftharpoons \overset{+}{N}H_4 + CH_3OH$$

6.25

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The better yield will be obtained by using the secondary halide, 1-bromo-1-phenylethane, because the desired reaction is E2. Using the primary halide will result in substantial S_N2 reaction as well, producing the alcohol as well as the desired alkene.

6.26

Reaction (2) would give the better yield because the desired reaction is an S_N2 reaction, and the substrate is a methyl halide. Use of reaction (1) would, because the substrate is a secondary halide, result in considerable elimination by an E2 pathway.

General S_N1, S_N2, and Elimination

6.27

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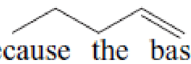
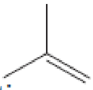
(a) The major product would be (by an S_N2 mechanism) because the substrate is primary and the nucleophile-base is not hindered. Some would be produced by an E2 mechanism.

(b) The major product would be  (by an E2 mechanism), even though the substrate is primary, because the base is a hindered strong base. Some would be produced by an S_N2 mechanism.

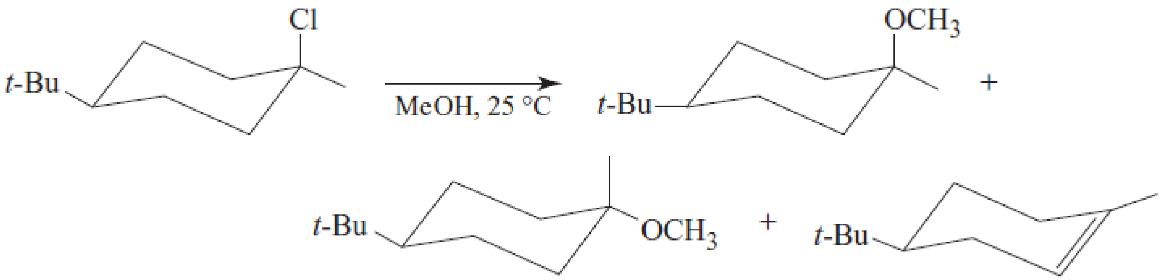
(c) For all practical purposes,  (by an E2 mechanism) would be the only product because the substrate is tertiary and the base is strong.

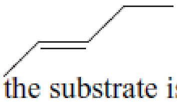
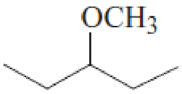
(d) Same answer as (c) above.

(e)

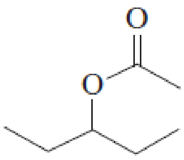
(formed by an S_N2 mechanism) would, for all practical purposes, be the only product. Iodide ion is a very weak base and a good nucleophile.

(f) Because the substrate is tertiary and the base weak, an S_N1 reaction (solvolysis) will occur, accompanied by elimination (E1). At 25°C, the S_N1 reaction would predominate.

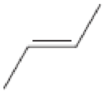
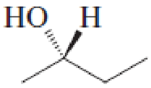


(g)  [also (*Z*)] (by an E2 mechanism) would be the major product because the substrate is secondary and the base/nucleophile is a strong base. Some of the ether 

would be formed by an S_N2 pathway.

(h) The major product would be 

(by an S_N2 mechanism) because the acetate ion is a weak base. Some and might be formed by an E2 pathway.

(i)  [also (*Z*)] and (by E2) would be major products, and 

[(*S*) isomer] (by S_N2) would be the minor product.

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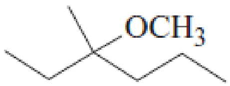
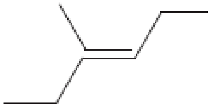
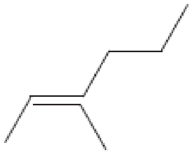
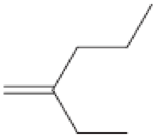
(j) 

(by S_N1) would be the major product.  [also (*Z*)],

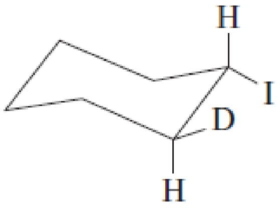
 [also (*Z*)], and  (by E1) would be minor products.

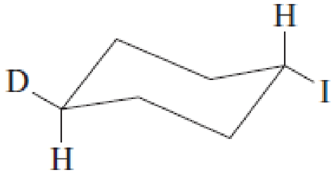
(k)

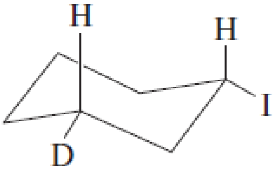
(by S_N2) would be the only product.

6.28

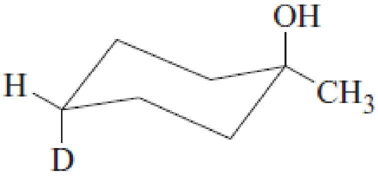
(a), (b), and (c) are all S_N2 reactions and, therefore, proceed with inversion of configuration. The products are

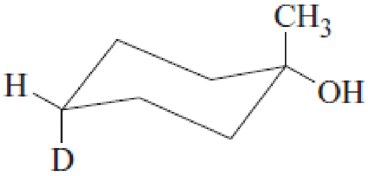
(a) 

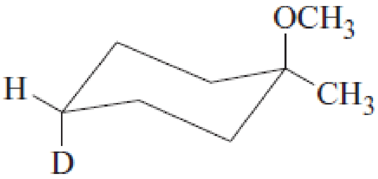
(b) 

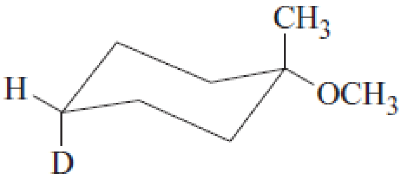
(c) 

(d) is an S_N1 reaction. The carbocation that forms can react with either nucleophile (H_2O or CH_3OH) from either the top or bottom side of the molecule. Four substitution products (below) would be obtained. (Considerable elimination by an E1 path would also occur.)



and




and


6.29

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(a) S_N2 because the substrate is a 1° halide.

(b) Rate $= k\,[CH_3CH_2Cl][I^-]$

$$= 5 \times 10^{-5}\ \text{L mol}^{-1}\text{s}^{-1} \times 0.1\ \text{mol L}^{-1} \times 0.1\ \text{mol L}^{-1}$$

Rate $= 5 \times 10^{-7}$ mol $L^{-1}s^{-1}$

(c) 1×10^{-6} mol $L^{-1}s^{-1}$

(d) 1×10^{-6} mol $L^{-1}s^{-1}$

(e) 2×10^{-6} mol $L^{-1}s^{-1}$

6.30

(a) $CH_3\bar{N}H$ because it is the stronger base.

(b) CH_3O^- because it is the stronger base.

(c) CH_3SH because sulfur atoms are larger and more polarizable than oxygen atoms.

(d) $(C_6H_5)_3P$ because phosphorus atoms are larger and more polarizable than nitrogen atoms.

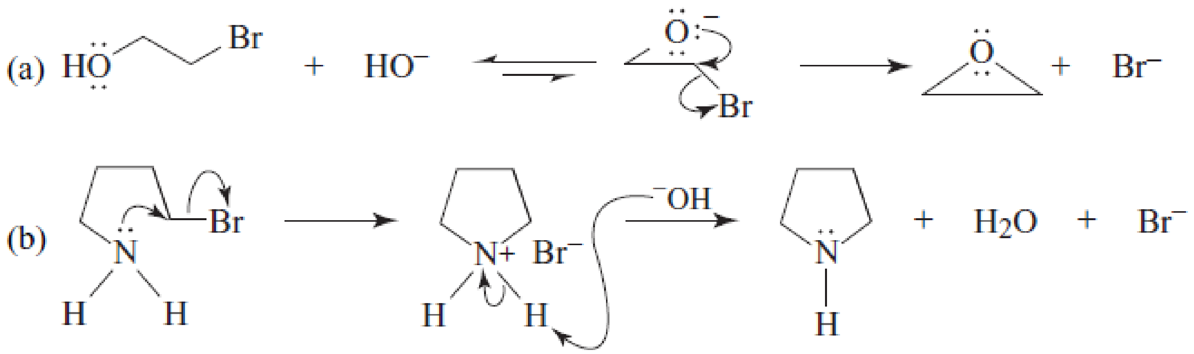
(e) H_2O because it is the stronger base.

(f) NH_3 because it is the stronger base.

(g) HS^- because it is the stronger base.

(h) HO^- because it is the stronger base.

6.31



6.32

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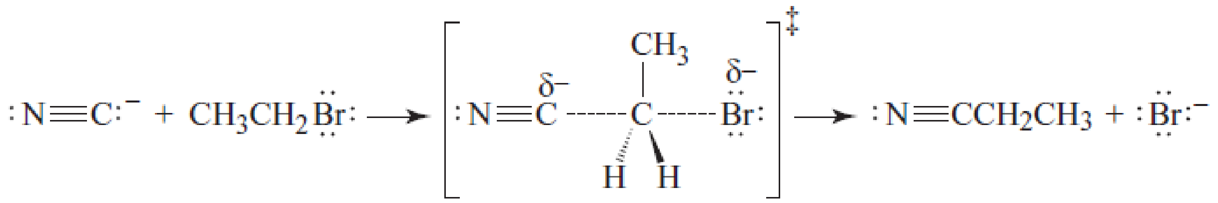
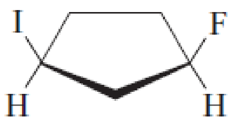


6.33

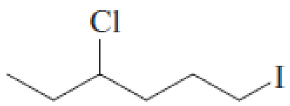
(a) You should use a strong base, such as RO^-, at a higher temperature to bring about an E2 reaction.

(b) Here we want an S_N1 reaction. We use ethanol as the solvent *and as the nucleophile*, and we carry out the reaction at a low temperature so that elimination will be minimized.

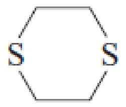
6.34

(a) 

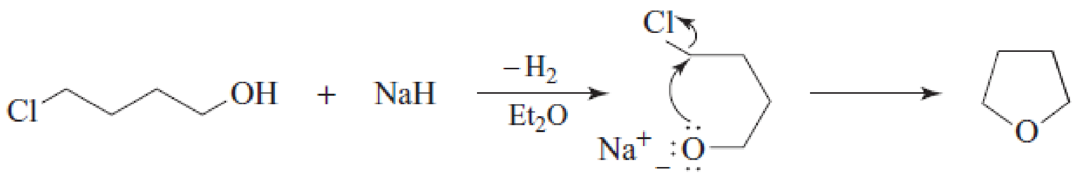
(Formation of this product depends on the fact that bromide ion is a much better leaving group than fluoride ion.)

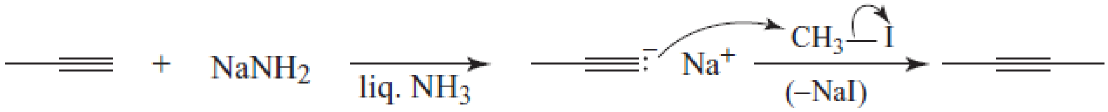
(b) 

(Formation of this product depends on the greater reactivity of 1° substrates in S_N2 reactions.)

(c) 

(Here two S_N2 reactions produce a cyclic molecule.)

(d) 

(e) 

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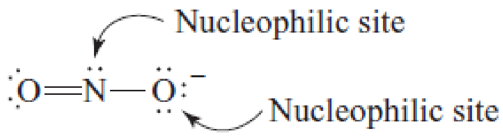
6.35

The nitrite ion is an *ambident nucleophile*; that is, it is an ion with two nucleophilic sites. The equivalent oxygen atoms and the nitrogen atom are nucleophilic.



6.36

(a) The transition state has the form:

$$\overset{\delta^+}{\text{Nu}}\text{----R-----}\overset{\delta^-}{\text{L}}$$

in which charges are developing. The more polar the solvent, the better it can solvate the transition state, thus lowering the free energy of activation and increasing the reaction rate.

(b) The transition state has the form:

$$\overset{\delta^+}{\text{R}}\text{---------}\overset{\delta^+}{\text{L}}$$

in which the charge is becoming dispersed. A polar solvent is less able to solvate this transition state than it is to solvate the reactant. The free energy of activation, therefore, will become somewhat larger as the solvent polarity increases, and the rate will be slower.

6.37

(a)

(b)

+ some alkene

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (a) The S_N1 reaction is faster in option (a) due to more stable carbocation.

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2. (c) Larger sized anion is better nucleophile due to lesser solvation.
3. (a) In S_N1, rate depends upon the alkyl halide concentration only.

4. (a) The order is according to leaving group.
5. (a) The order is according to the stability of carbocation formed in the rds step in S_N1.

6. (c) The product would be racemic in S_N1.

7. (d) The order is according to leaving group tendency.
8. (a) Electron donating group –OCH_3 would increase the rate of S_N1 due to stabilization of carbocation in rds step.

9. (d) **Correction!! Both reactions given are same.**

10. (b) Rearrangement of carbocation will take place to benzylic position.

11. (a) Order is on the basis of stability of carbocation in the transition state.

12. (c) The solvent must have a balance between the stability of carbocation due to solvation by water and allowing nucleophile to attack carbocation for racemization.

13. (d) The negative charge is most stabilized due to large size of I.
14. (a) Substitution of good leaving group Br will take place.

15. (d) Aryl halide won't undergo substitution due to strong C-halogen bond and less stable aryl carbocation.

16. (a)

17. (d) Rate depends upon all the factors.
18. (c) It is used in elimination reaction of halogens.
19. (d) Reaction has no intermediate and the product is more stable due to replacement of weak C-I bond wit stronger C-N bond.

20. (d) Due to less solvation of iodide ion.
21. (b) Due to the most stable carbocation.

23. (d) S_N2 (Finkelstein Reaction).

24. (a) Fluoride ion high negative charge density.
25. (c) Both would give allylic cyclohexene product.

<H2> Integer Type

1. (1) E2 reaction gives anti elimination.

<H2> Matrix Match Type

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1. $a \to (p, q, r, s, t); b \to (p, s, t); c \to (p, q, r, t); d \to (p)$

Option (a) has secondary benzylic halide which can give all given types of reaction.

Option (b) will not give elimination as no β H.

Option (c) will not give S_N2 due to steric hindrance.

Option (d) will give S_NAr reaction.

2. $a \to (p, r); b \to (p, r); c \to (p, r); d \to (q, r)$

Option (a): It is E2 reaction and the lower Cl atom will be eliminated to yield conjugated diene.

Option (b): It is E2 reaction and the lower Cl atom would be eliminated alongside H atom from C to which the middle Cl is attached.

Option (c): It is S_N2 reaction and the Cl will be substituted with OH.

Option (d): It is S_N2 reaction and the Cl will be substituted with OH. The product would have a plane of symmetry.

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Chapter 7: Alkenes and Alkynes I: Properties and Synthesis. Elimination Reactions of Alkyl Halides

Practice Problems

7.1

(a) (*E*)-1-Bromo-1-chloro-1-pentene or (*E*)-1-Bromo-1-chloropent-1-ene

(b) (*E*)-2-Bromo-1-chloro-1-iodo-1-butene or (*E*)-2-Bromo-1-chloro-1-iodobut-1-ene

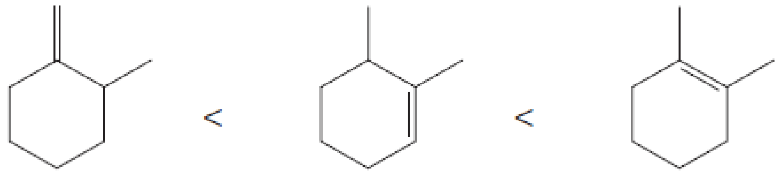
(c) (*Z*)-3,5-Dimethyl-2-hexene or (*Z*)-3,5-Dimethylhex-2-ene

(d) (*Z*)-1-Chloro-1-iodo-2-methyl-1-butene or (*Z*)-1-Chloro-1-iodo-2-methylbut-1-ene

(e) (*Z*,4*S*)-3,4-Dimethyl-2-hexene or (*Z*,4*S*)-3,4-Dimethylhex-2-ene

(f) (*Z*,3*S*)-1-Bromo-2-chloro-3-methyl-1-hexene or
(*Z*,3*S*)-1-Bromo-2-chloro-3-methylhex-1-ene

7.2



Order of increasing stability

7.3

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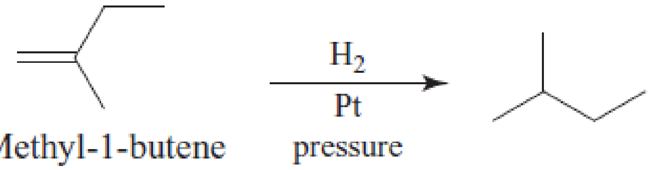
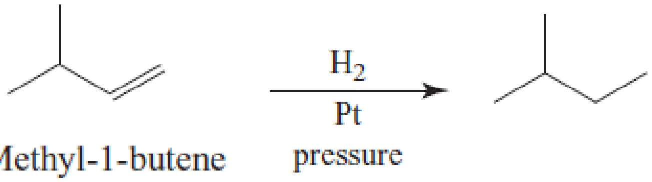
(a), (b)



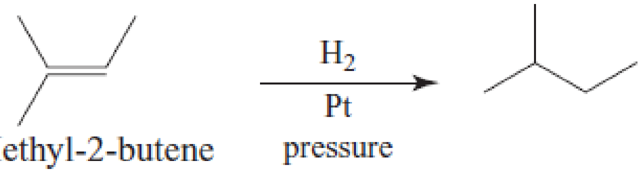
2-Methyl-1-butene (disubstituted)

$\Delta H° = -119 \text{ kJ mol}^{-1}$



3-Methyl-1-butene (monosubstituted)

$\Delta H° = -127 \text{ kJ mol}^{-1}$

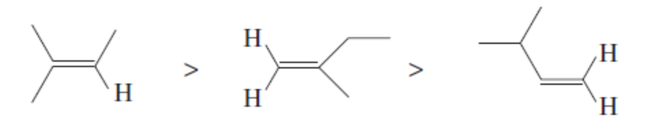


2-Methyl-2-butene (trisubstituted)

$\Delta H° = -113 \text{ kJ mol}^{-1}$

(c) Yes, because hydrogenation converts each alkene into the same product.

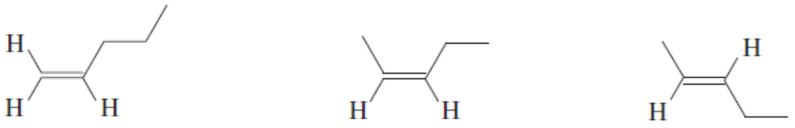
(d)



(trisubstituted) > (disubstituted) > (monosubstituted)

Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

(e)



1-Pentene   *cis*-2-Pentene   *trans*-2-Pentene

(f) Order of stability: *trans*-2-pentene > *cis*-2-pentene > 1-pentene

7.4

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(a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetra-substituted. 2-Methyl-2-pentene has a trisubstituted double bond.

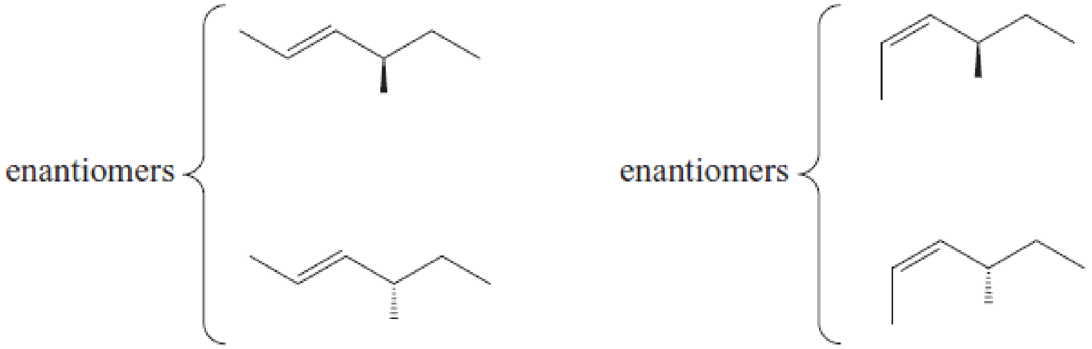
(b) *trans*-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.

(c) *cis*-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.

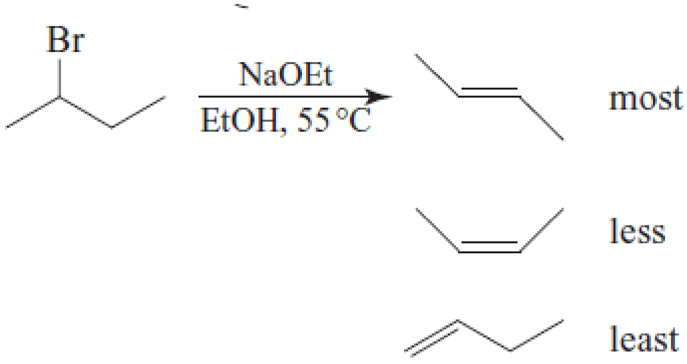
(d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of *trans*-2-hexene is disubstituted.

7.5

Four stereoisomers. However only *two fractions* are found as enantiomer pairs are indistinguishible by distillation.



7.6



7.7

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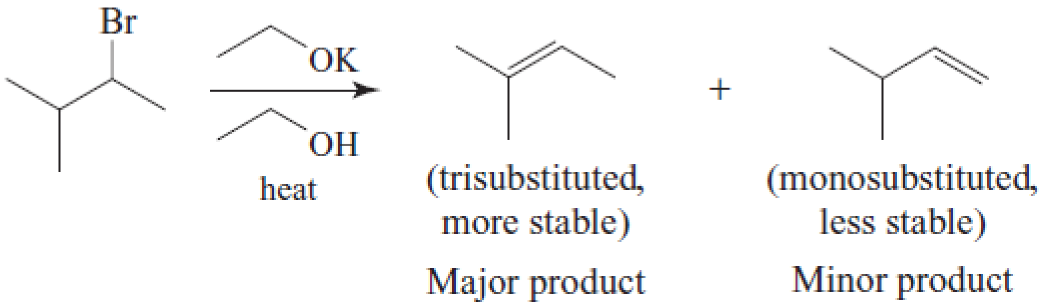
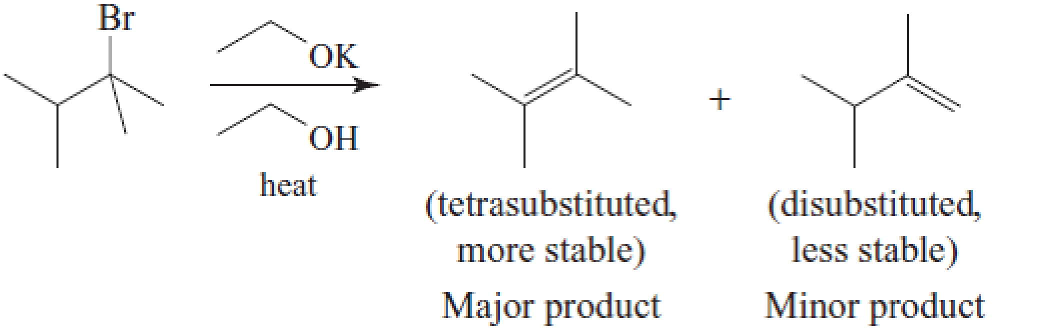
(a)



(b)



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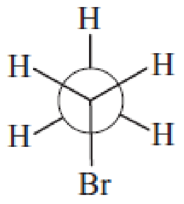
7.8

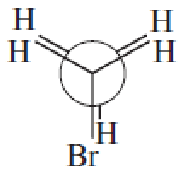
t-BuOK in *t*-BuOH

7.9

An anti coplanar transition state allows the molecule to assume the more stable staggered conformation,



whereas a syn coplanar transition state requires the molecule to assume the less stable eclipsed conformation.



7.10

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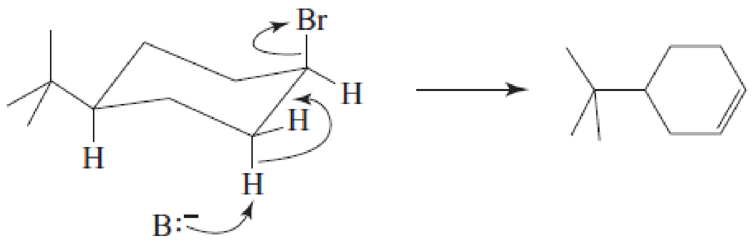
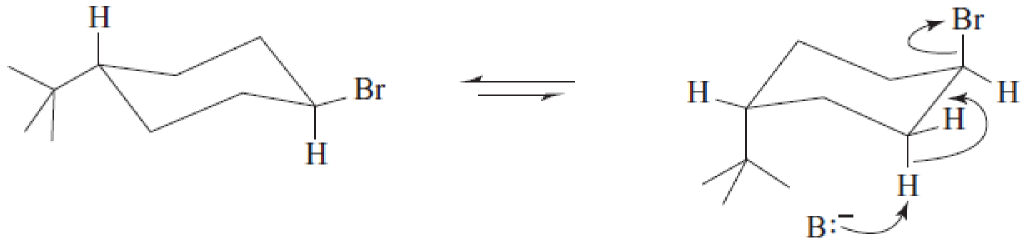
cis-1-Bromo-4-*tert*-butylcyclohexane can assume an anti coplanar transition state in which the bulky *tert*-butyl group is equatorial.



The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

On the other hand, for *trans*-1-bromo-4-*tert*-butylcyclohexane to assume an anti coplanar transition state, the molecule must assume a conformation in which the large *tert*-butyl group is axial:



Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

7.11

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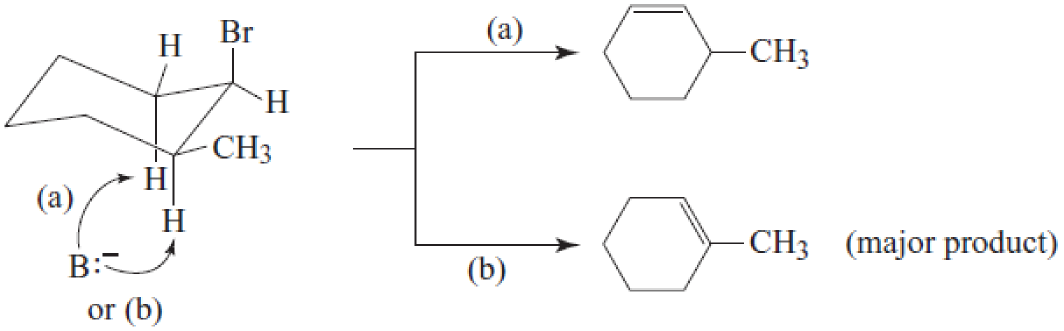
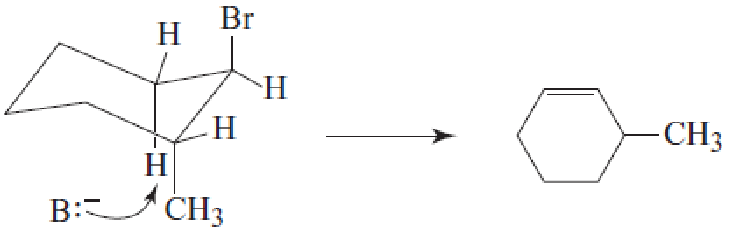
(a) Anti coplanar elimination can occur in two ways with the cis isomer.



cis-1-Bromo-2-methylcyclohexane

(b) Anti coplanar elimination can occur in only one way with the trans isomer.



trans-1-Bromo-2-methylcyclohexane

7.12

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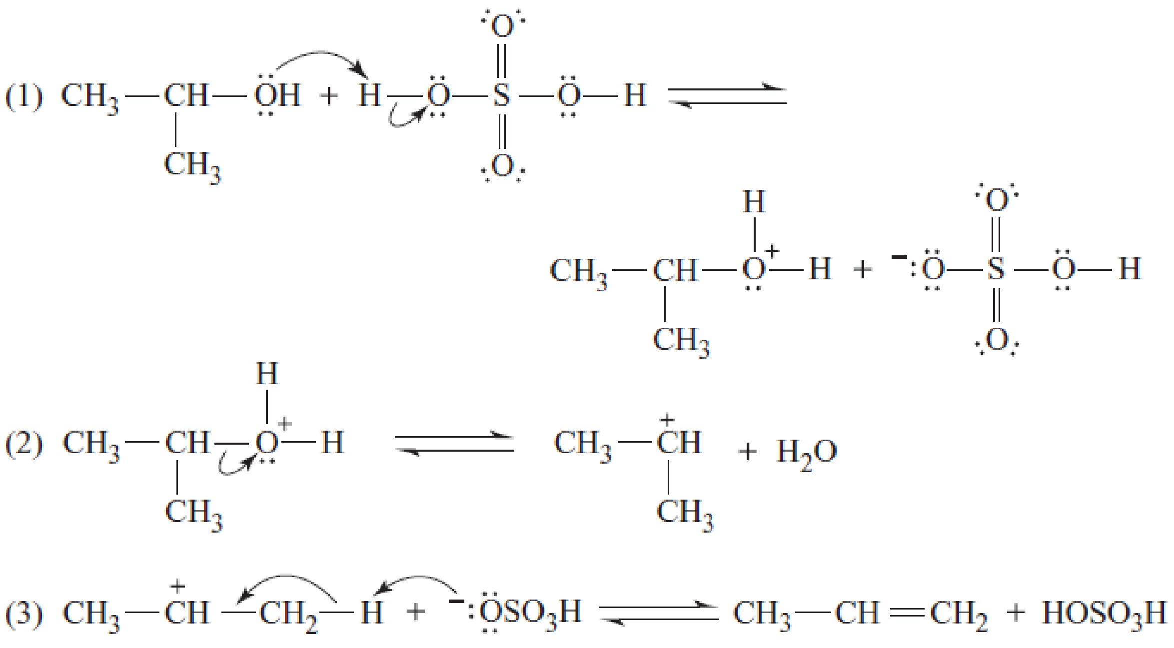
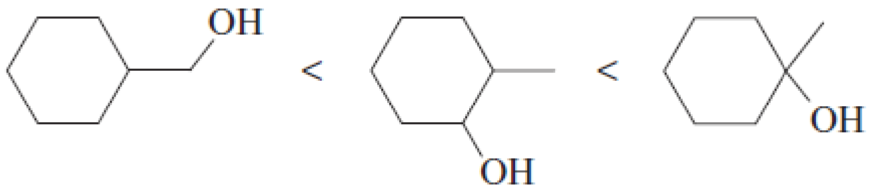
(a)



(b) By donating a proton to the —OH group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group (H_2O) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic HO^- ion, and such steps almost never occur.

7.13



1° < 2° < 3°

Order of increasing case of dehydration

7.14

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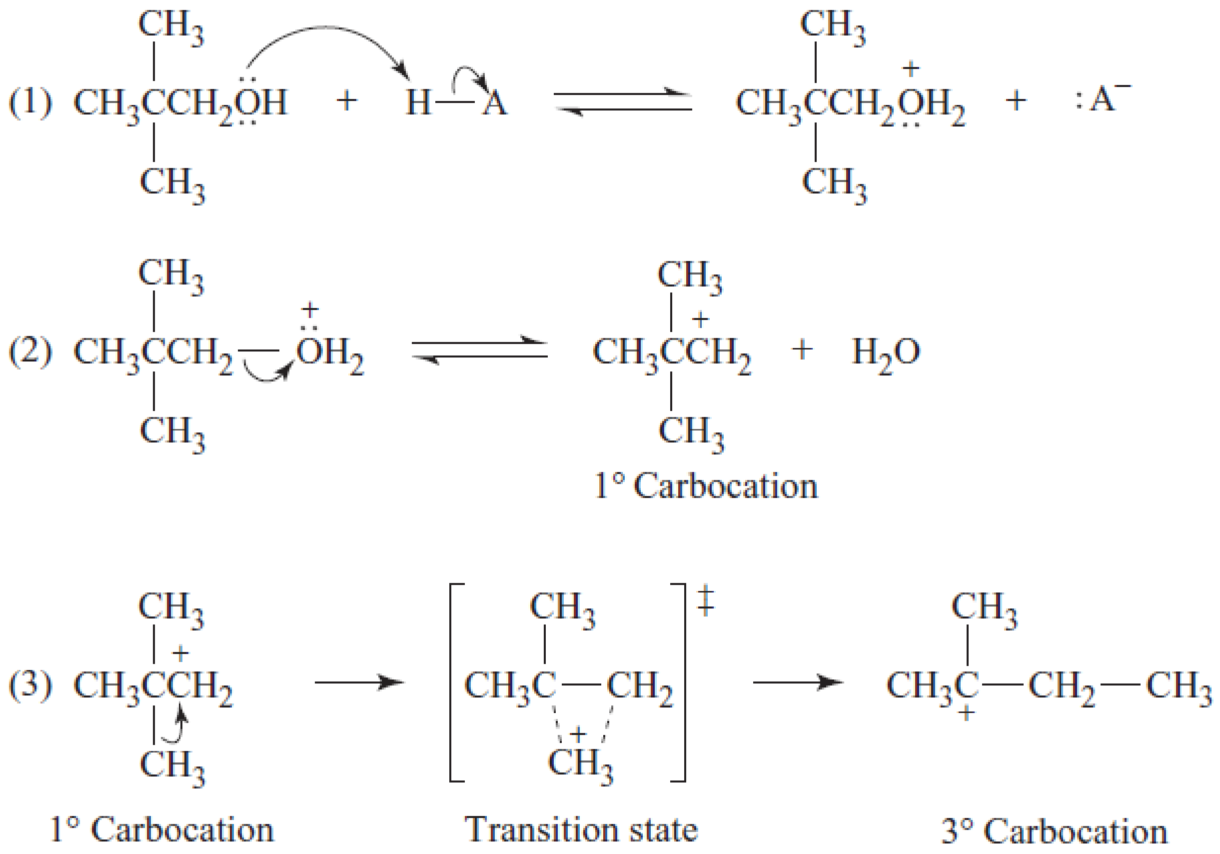
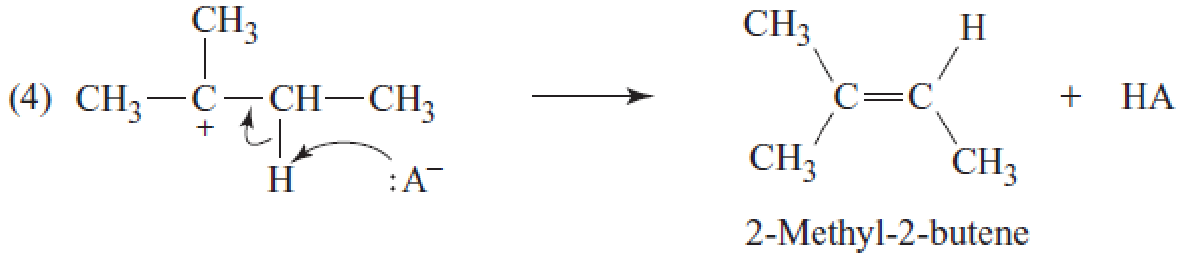


[Steps (2) and (3), ionization and rearrangement, may occur simultaneously.]



7.15

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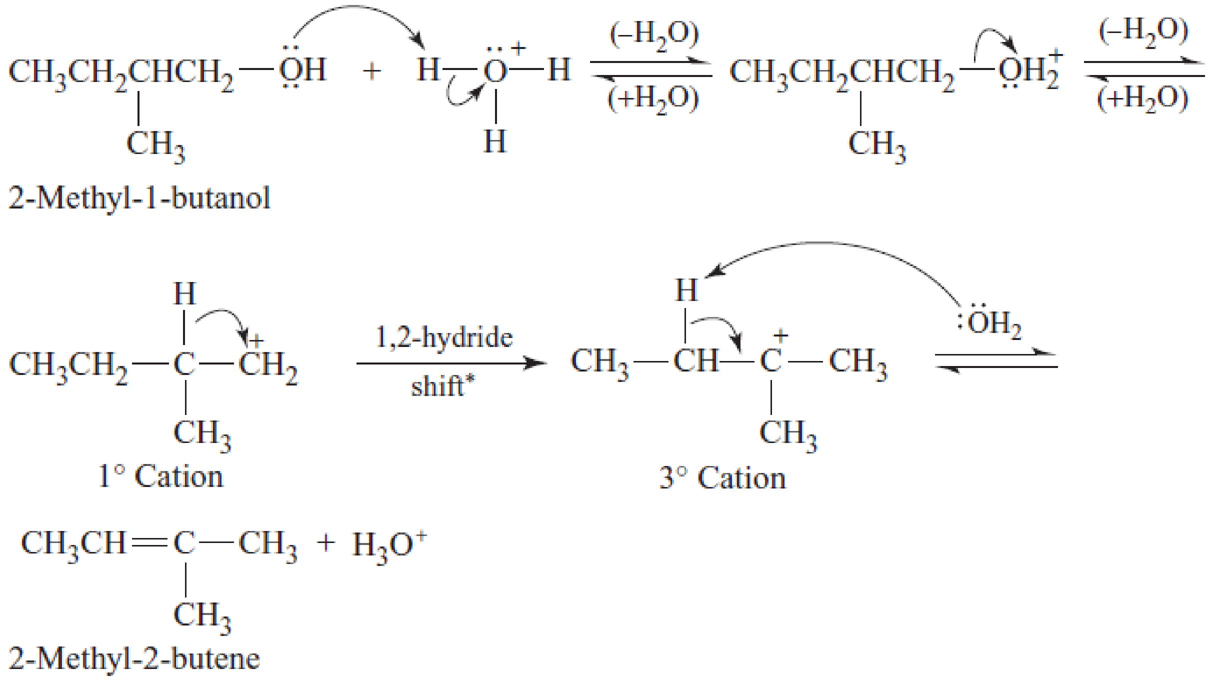

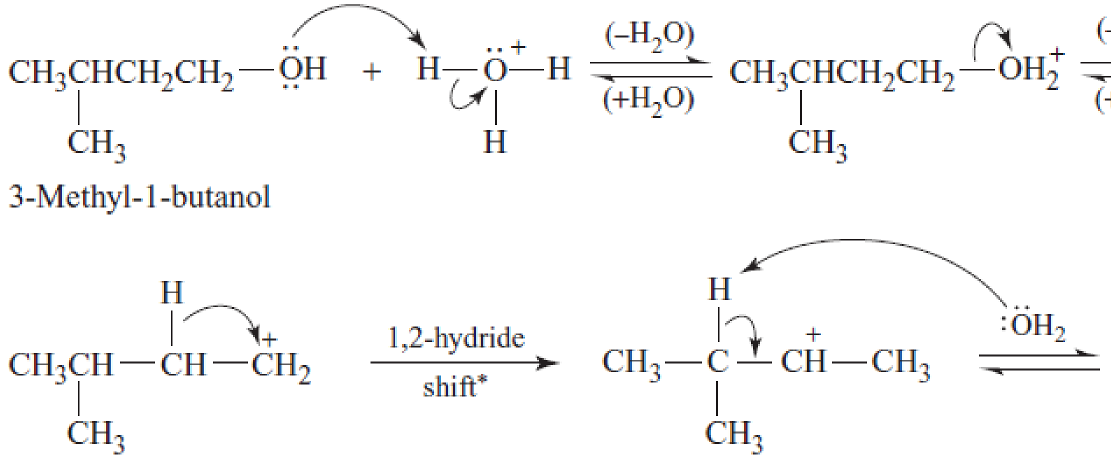

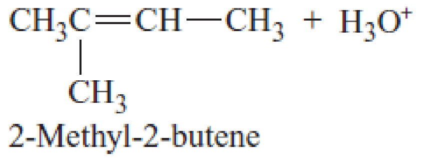

* The hydride shift may occur simultaneously with the preceding step.

7.16

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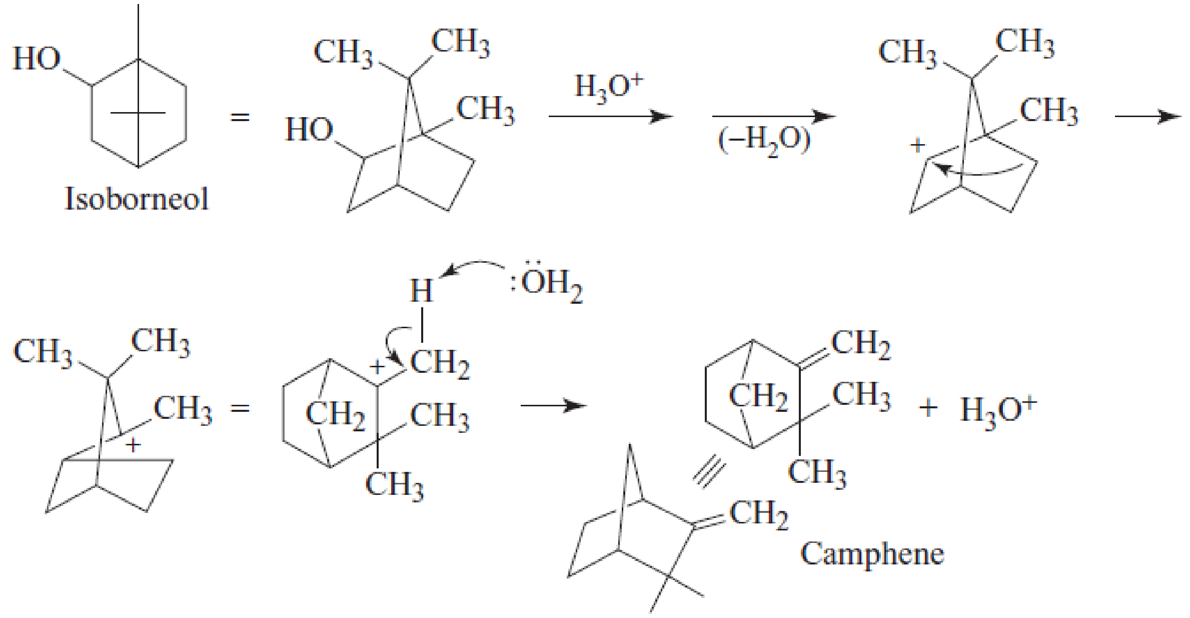

7.17

(a) $CH_3CH{=}CH_2 + NaNH_2 \longrightarrow$ No reaction

(b) $CH_3C{\equiv}C{-}H + Na^+ \; ^-{:}\ddot{N}H_2 \longrightarrow CH_3C{\equiv}C{:}^- Na^+ + {:}NH_3$

Stronger acid; Stronger base; Weaker base; Weaker acid

(c) $CH_3CH_2CH_3 + NaNH_2 \longrightarrow$ No reaction

(d) $CH_3C{\equiv}C{:}^- + H{-}\ddot{O}CH_2CH_3 \longrightarrow CH_3C{\equiv}CH + ^-{:}\ddot{O}CH_2CH_3$

Stronger base; Stronger acid; Weaker acid; Weaker base

(e) $CH_3C{\equiv}C{:}^- + H{-}\overset{+}{N}H_3 \longrightarrow CH_3C{\equiv}CH + {:}NH_3$

Stronger base; Stronger acid; Weaker acid; Weaker base

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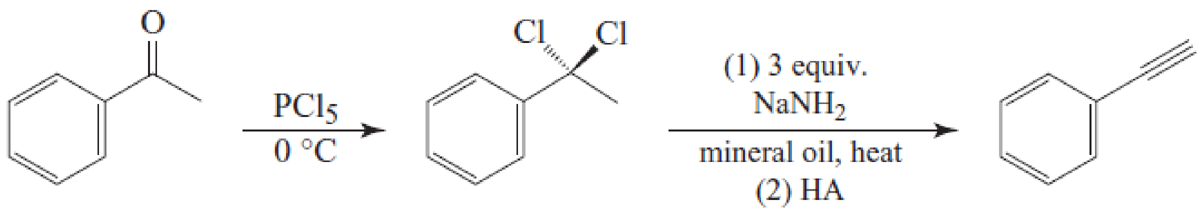
7.18



7.19

(a) $CH_3\overset{\overset{\large O}{\|}}{C}CH_3 \xrightarrow[0\ ^\circ C]{PCl_5} CH_3CCl_2CH_3 \xrightarrow[\substack{\text{mineral oil, heat}\\(2)\ NH_4^+}]{(1)\ 3\ NaNH_2} CH_3C{\equiv}CH$

(b) $CH_3CH_2CHBr_2 \xrightarrow[\substack{\text{mineral oil, heat}\\(2)\ NH_4^+}]{(1)\ 3\ NaNH_2} CH_3C{\equiv}CH$

(c) $CH_3CHBrCH_2Br \xrightarrow{[\text{same as (b)}]} CH_3C{\equiv}CH$

(d) $CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\underset{\underset{\large Br}{|}}{C}HCH_2Br \xrightarrow{[\text{same as (b)}]} CH_3C{\equiv}CH$

7.20

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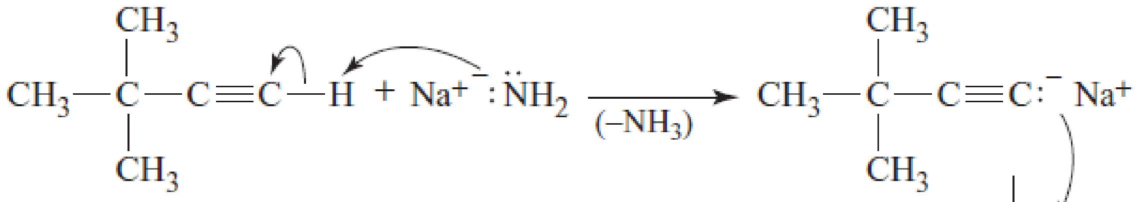
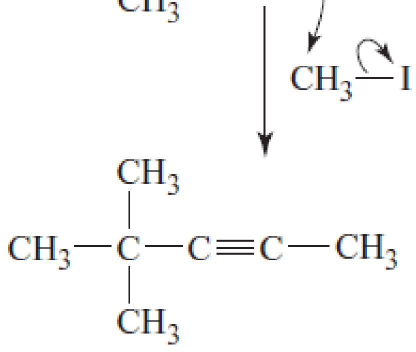


(Starting the synthesis with 1-propyne and attempting to alkylate with a *tert*-butyl substrate would not work because elimination would occur instead of substitution.)



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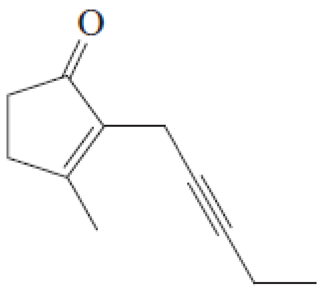

Compound A

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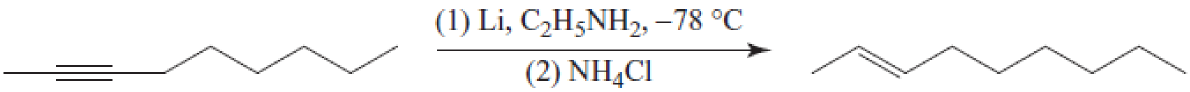
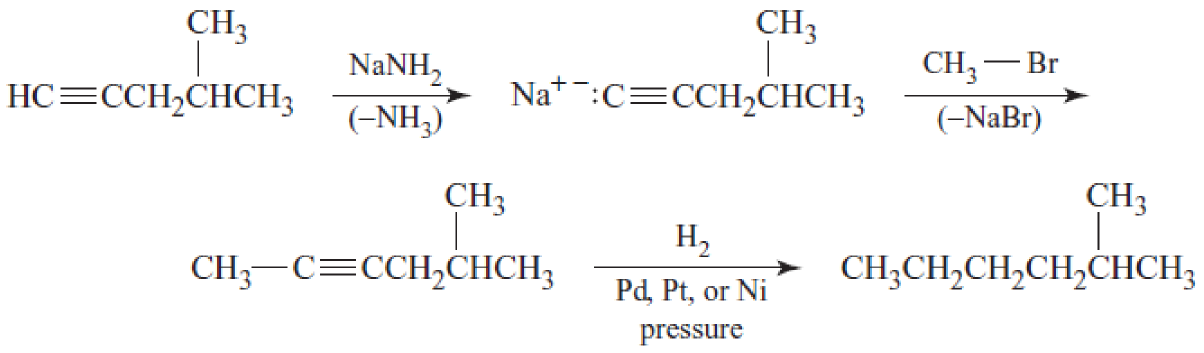
7.22



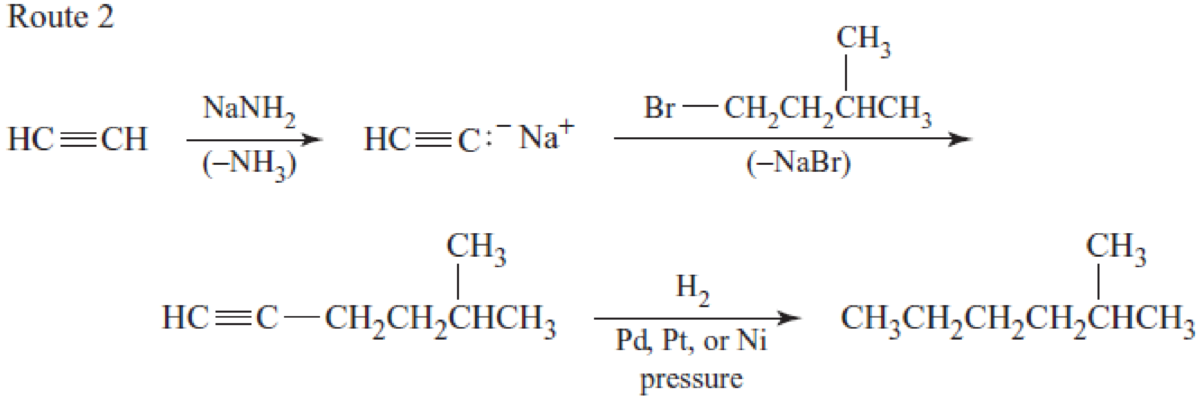
(E)-2-Nonene

7.23

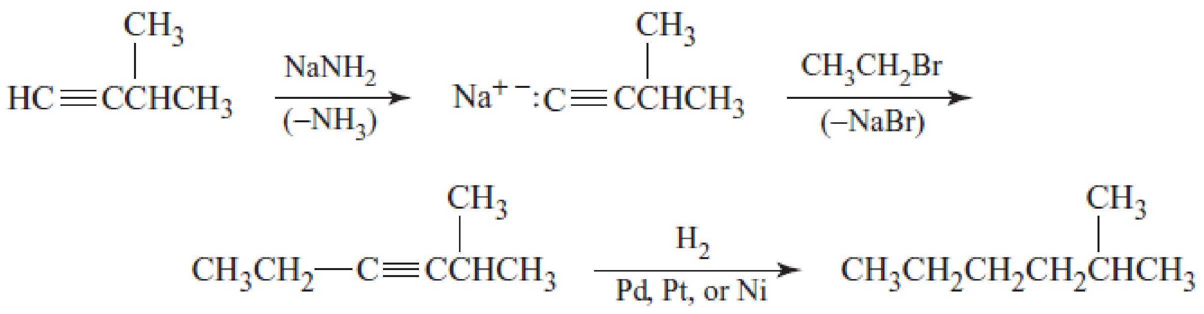
Route 1



Route 2

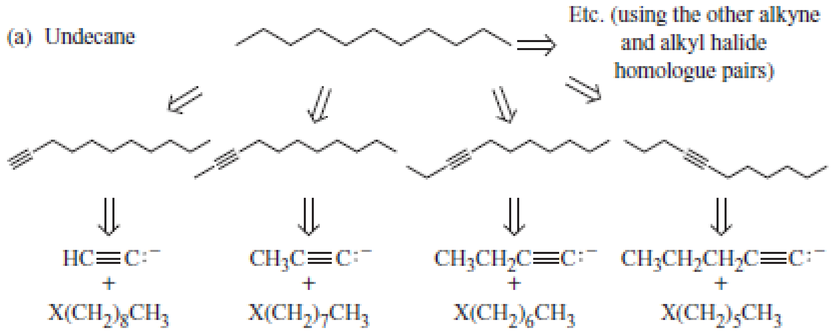


Route 3

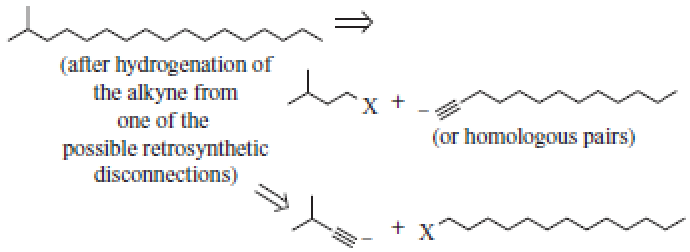


7.24

(a) Undecane



2-Methylheptadecane



(Note that is not a good choice because the alkyl halide is branched at the carbon adjacent to the one which bears the halogen. Neither would work because the alkyl halide is secondary. Both of these routes would lead to elimination instead of substitution.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be

$$RC{\equiv}C{-}H \xrightarrow[(-NH_3)]{NaNH_2} R{-}C{\equiv}C{:}^- \xrightarrow[\text{(R}' \text{ is primary and unbranched at the second carbon)}]{R'{-}X} R{-}C{\equiv}C{-}R' \xrightarrow[\text{Pd, Pt, or Ni, pressure}]{H_2} R{-}CH_2CH_2{-}R'$$

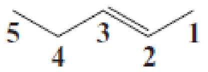
(a terminal alkyne; R = alkyl, H) (an alkynide anion)

Review Problems

Structure and Nomenclature

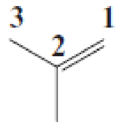
7.25

(a) We designate the position of the double bond by using the *lower* number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene.

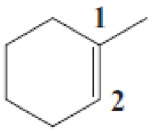


not

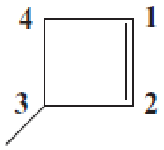
(b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.



(c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.



(d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.



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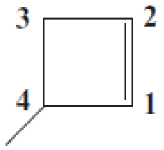
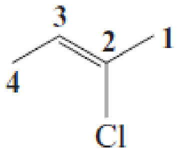


(e) We number in the way that gives the double bond *and the substituent* the lower number. The correct name is (Z)-2-chloro-2-butene or (Z)-2-chlorobut-2-ene.



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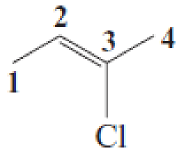
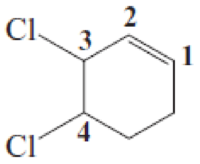
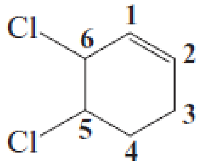


(f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.



not



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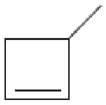
7.26

(a) 

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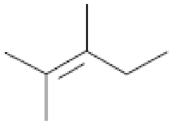
(c) 

(d)

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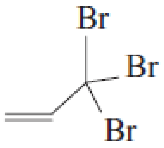
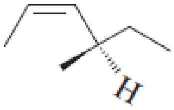
(f) 

(g) 

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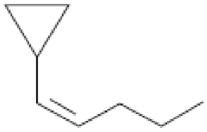
(i) 

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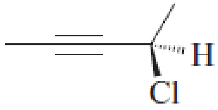
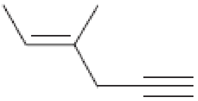
(k) 

(l) 

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7.27

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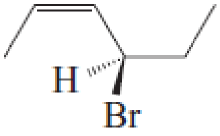
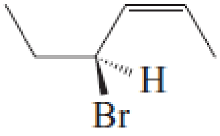
(a) 

(2*Z*,4*R*)-4-Bromo-2-hexene
or
(2*Z*,4*R*)-4-Bromohex-2-ene



(2*Z*,4*S*)-4-Bromo-2-hexene
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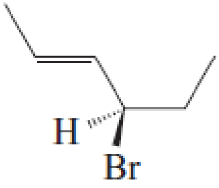
(2*Z*,4*S*)-4-Bromohex-2-ene



(2*E*,4*R*)-4-Bromo-2-hexene
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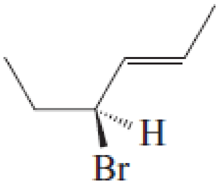
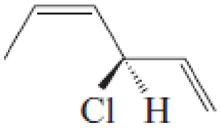
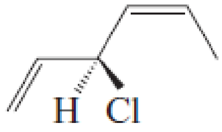


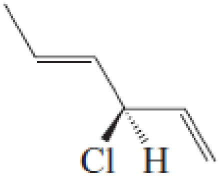
(2*E*,4*S*)-4-Bromo-2-hexene
or
(2*E*,4*S*)-4-Bromohex-2-ene

(b) 

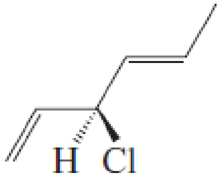
(3*R*,4*Z*)-3-Chloro-1,4-hexadiene
or
(3*R*,4*Z*)-3-Chlorohexa-1,4-diene



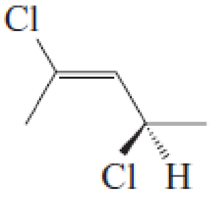
(3*S*,4*Z*)-3-Chloro-1,4-hexadiene
or
(3*S*,4*Z*)-3-Chlorohexa-1,4-diene



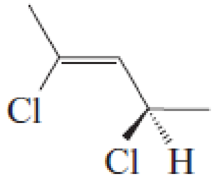
(3*R*,4*E*)-3-Chloro-1,4-hexadiene
or
(3*R*,4*E*)-3-Chlorohexa-1,4-diene



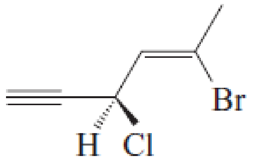
(3*S*,4*E*)-3-Chloro-1,4-hexadiene
or
(3*S*,4*E*)-3-Chlorohexa-1,4-diene

(c) 

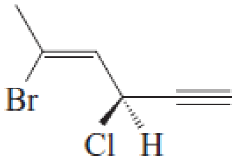
(2*E*,4*R*)-2,4-Dichloro-2-pentene
or
(2*E*,4*R*)-2,4-Dichloropent-2-ene



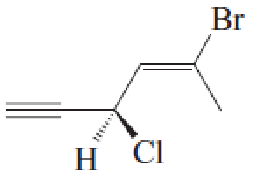
(2*Z*,4*R*)-2,4-Dichloro-2-pentene
or
(2*Z*,4*R*)-2,4-Dichloropent-2-ene

(d) 

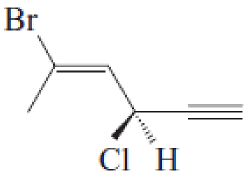
(3*R*,4*Z*)-5-Bromo-3-chloro-4-hexen-1-yne
or
(3*R*,4*Z*)-5-Bromo-3-chlorohex-4-en-1-yne



(3*S*,4*Z*)-5-Bromo-3-chloro-4-hexen-1-yne
or
(3*S*,4*Z*)-5-Bromo-3-chlorohex-4-en-1-yne



(3*R*,4*E*)-5-Bromo-3-chloro-4-hexen-1-yne
or
(3*R*,4*E*)-5-Bromo-3-chlorohex-4-en-1-yne



(3*S*,4*E*)-5-Bromo-3-chloro-4-hexen-1-yne
or
(3*S*,4*E*)-5-Bromo-3-chlorohex-4-en-1-yne

An IUPAC* rule covers those cases in which a double bond and a triple bond occur in the same molecule:

> Numbers as low as possible are given to double and triple bonds as a set, even though this may at times give "-yne" a lower number than "-ene." If a choice remains, preference for low locants is given to the double bonds.

*International Union of Pure and Applied Chemistry, www.iupac.org.

7.28

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(a) (*E*)-3,5-Dimethyl-2-hexene or (*E*)-3,5-dimethylhex-2-ene

(b) 4-Chloro-3-methylcyclopentene

(c) 6-Methyl-3-heptyne or 6-methylhept-3-yne

(d) 1-*sec*-Butyl-2-methylcyclohexene or 1-methyl-2-(1-methylpropyl)cyclohexene

(e) (4*Z*,3*R*)-3-Chloro-4-hepten-1-yne or (4*Z*,3*R*)-3-chlorohept-4-en-1-yne

(f) 2-Pentyl-1-heptene or 2-pentylhept-1-ene

7.29

1-Pentanol > 1-pentyne > 1-pentene > pentane
(See Section 3.8 for the explanation.)

Synthesis

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7.30

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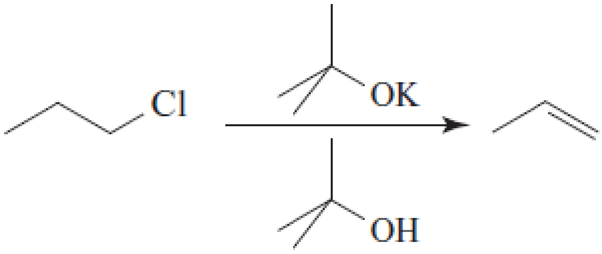
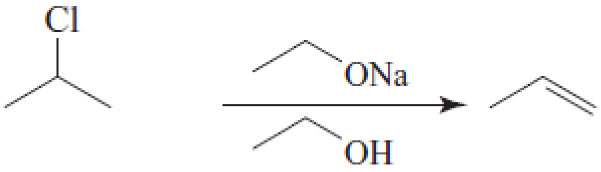
(a) 

(b) 

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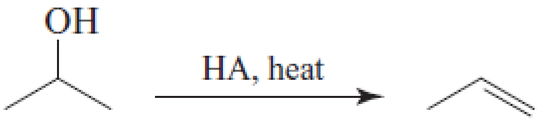
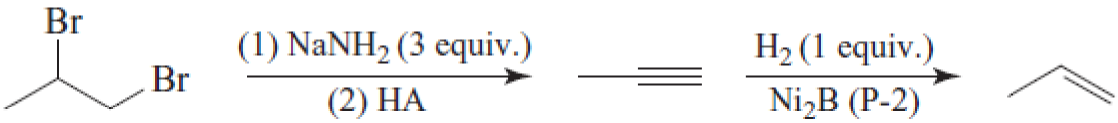
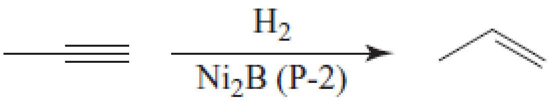
(d) 

(e) 

(f) 

7.31

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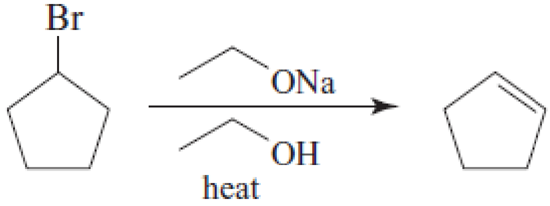
(a)



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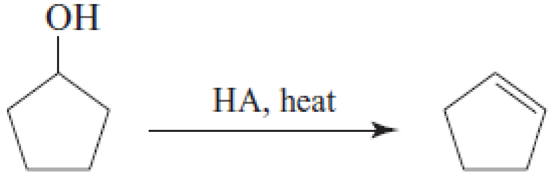

7.32

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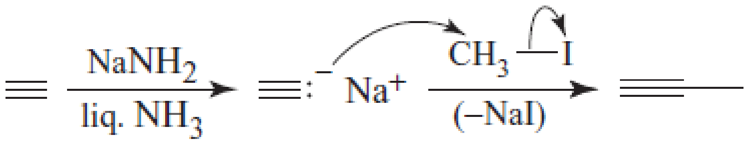
(a) 

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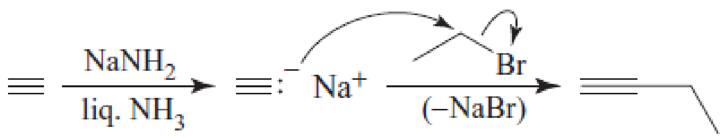

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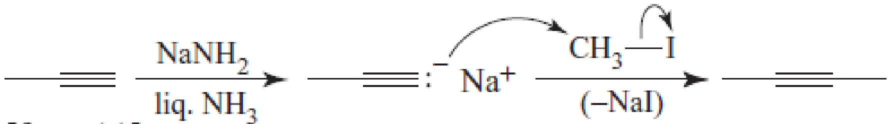

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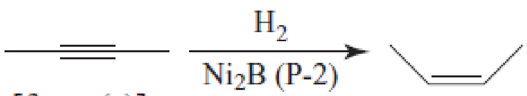

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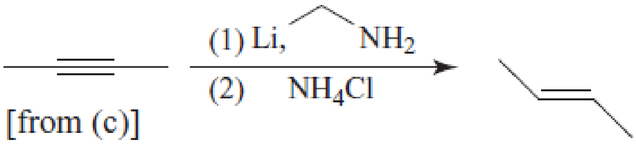

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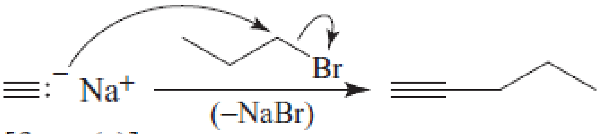

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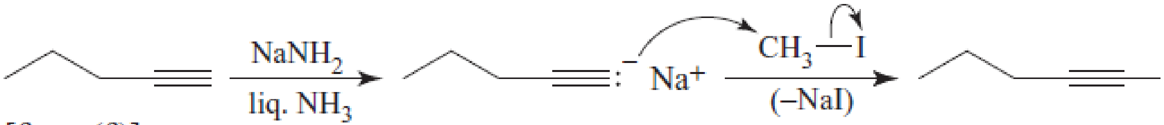

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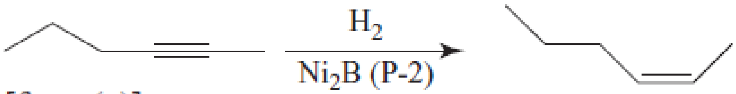

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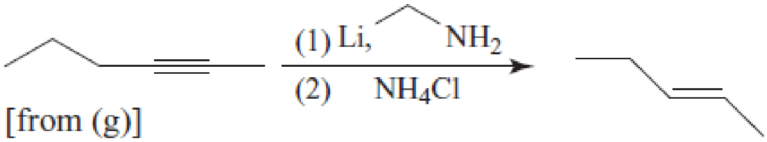

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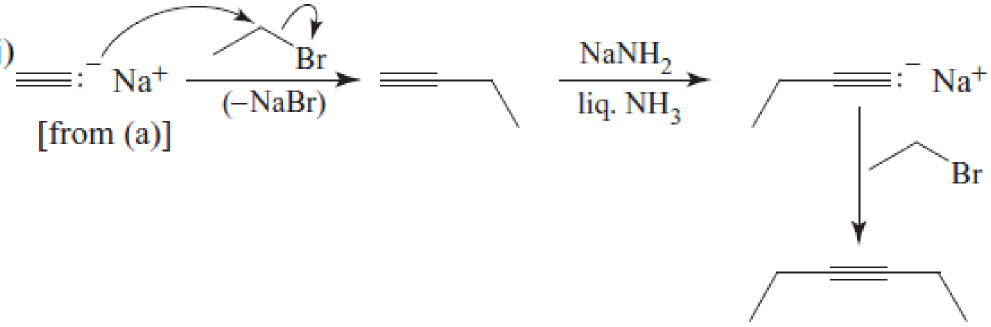

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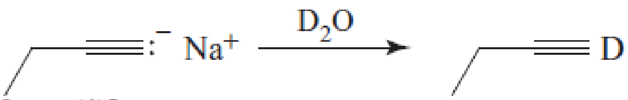

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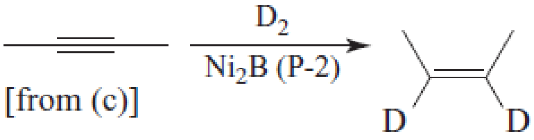

[from (c)]

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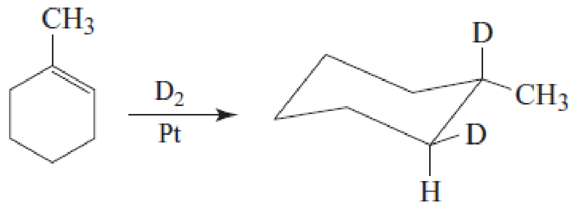
7.33

We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use D_2 and a metal catalyst (Section 7.14)



7.34

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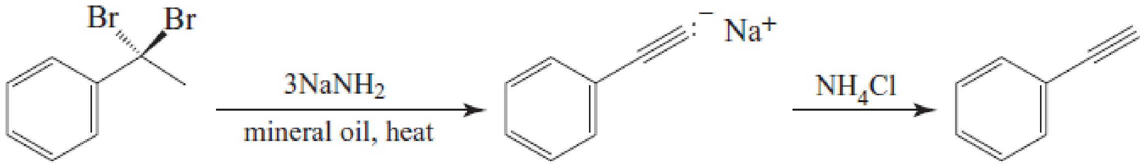
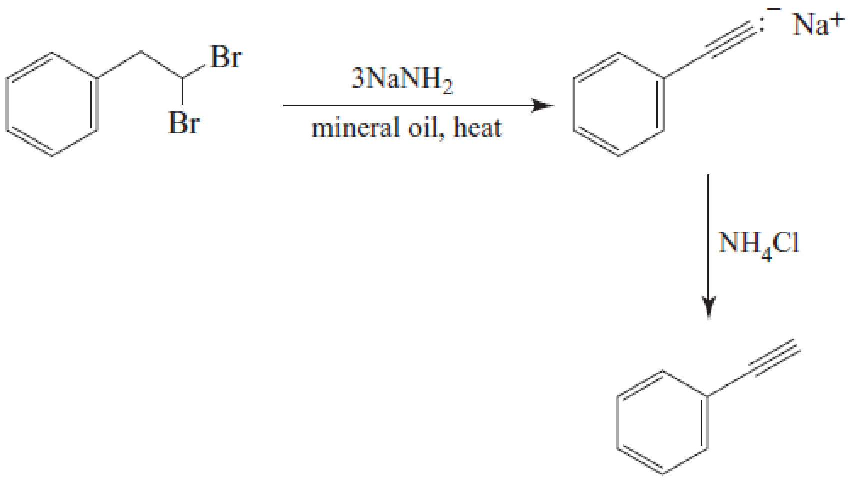
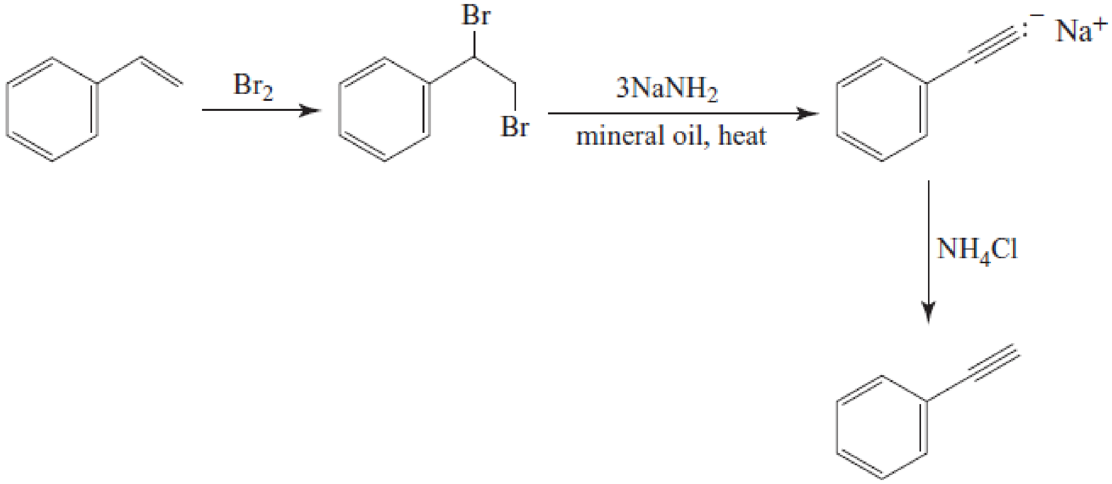
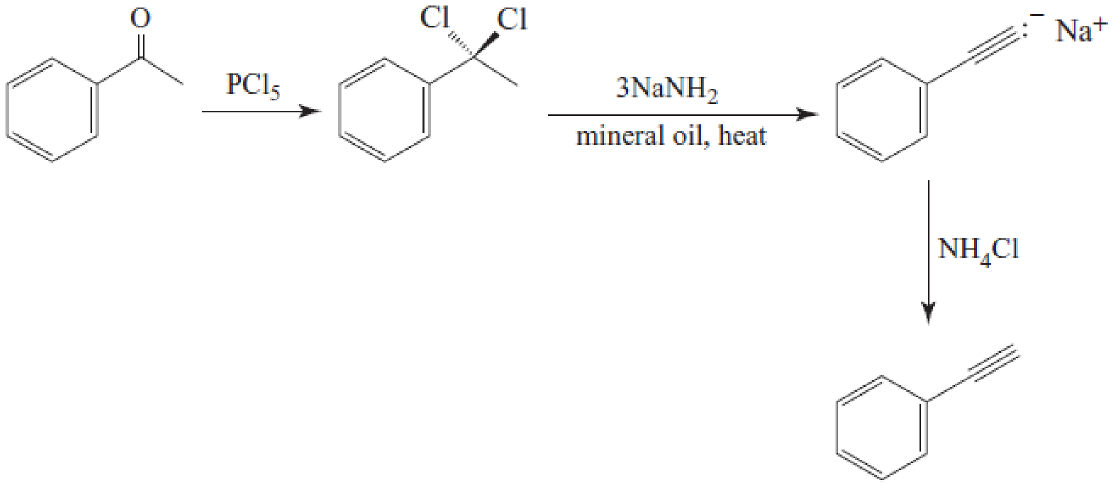
(a) 

(b) 

(c) 

(d) 

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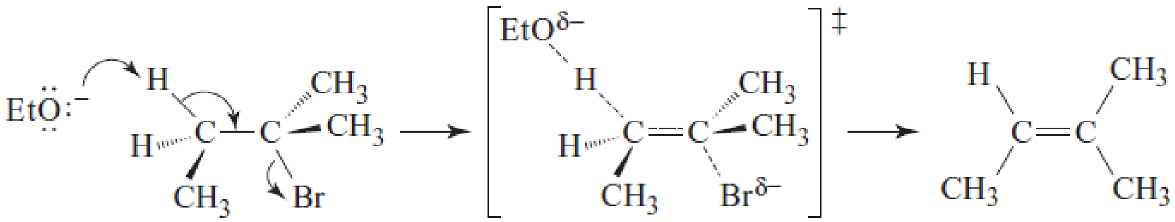
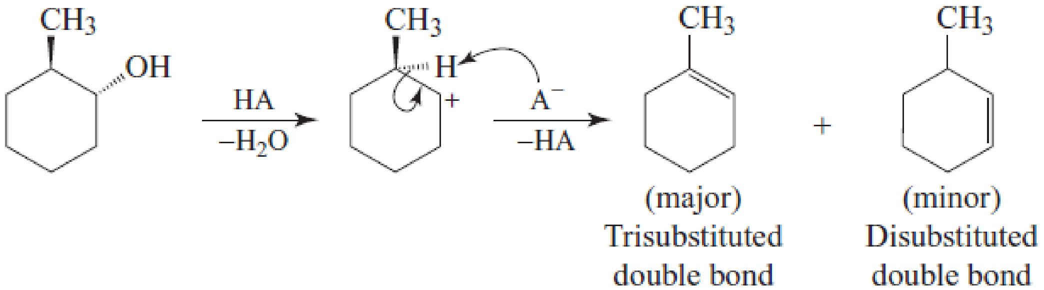
Dehydrohalogenation and Dehydration

7.35

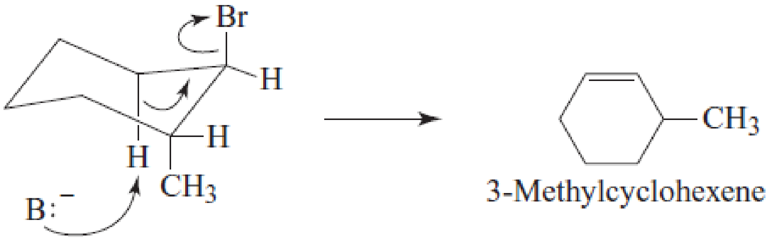


7.36

Dehydration of *trans*-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) because its double bond is more highly substituted.



Dehydrohalogenation of *trans*-1-bromo-2-methylcyclohexane is an E2 reaction and must proceed through an anti coplanar transition state. Such a transition state is possible only for the elimination leading to 3-methylcyclohexene (cf. Review Problem 7.11).



7.37

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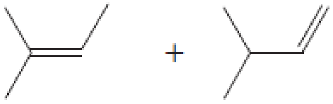
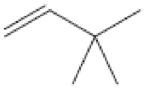
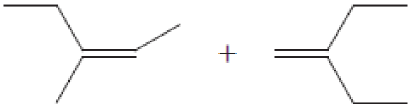
(a) 

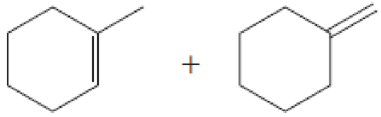
major + minor

(b) 

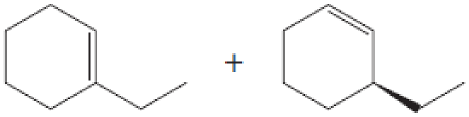
only product

(c) 

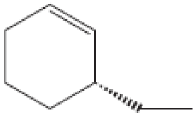
major (+ stereoisomer) + minor

(d) 

major + minor

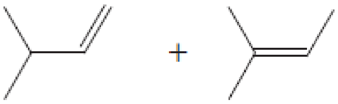
(e) 

major + minor

(f) 

only product

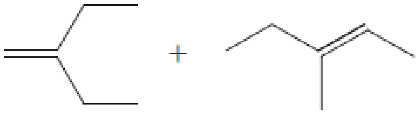
7.38

(a) 

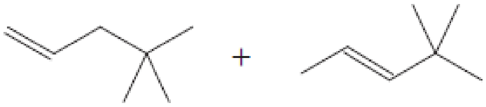
major + minor

(b)

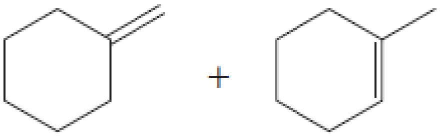
only product

(c) 

major + minor (+ stereoisomer)

(d) 

major + minor (+ stereoisomer)

(e) 

major + minor

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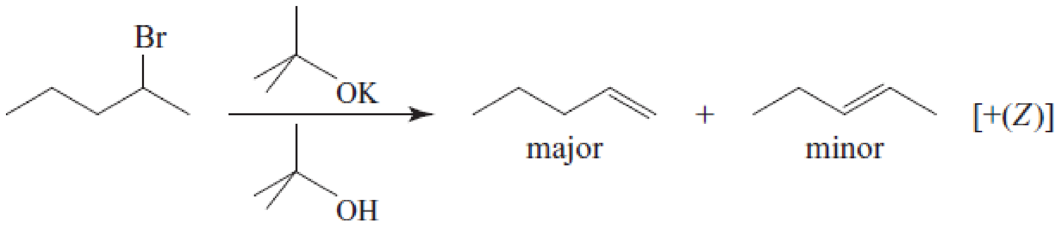
7.39

(a)



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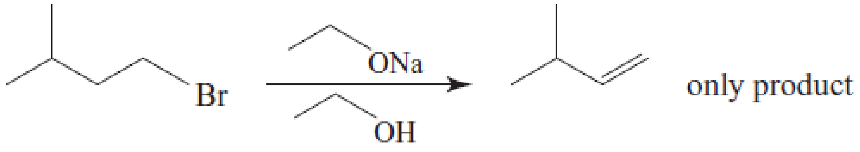

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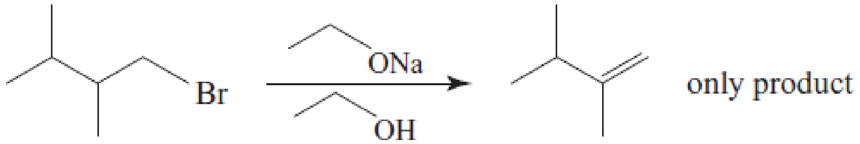

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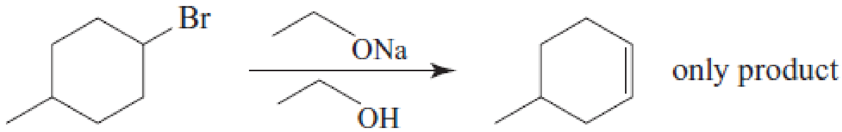
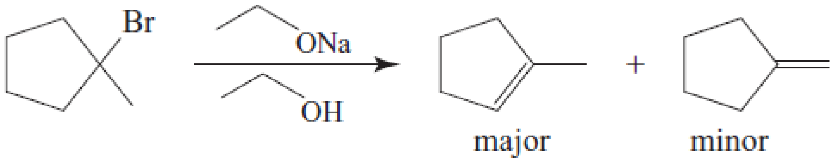


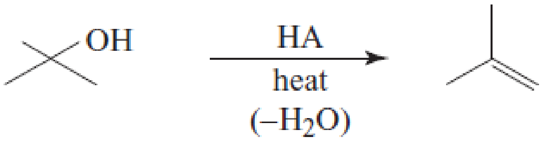
(e)

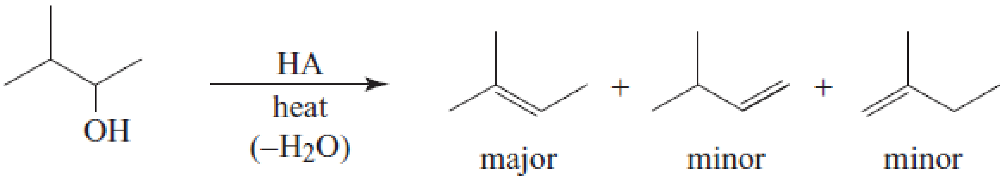


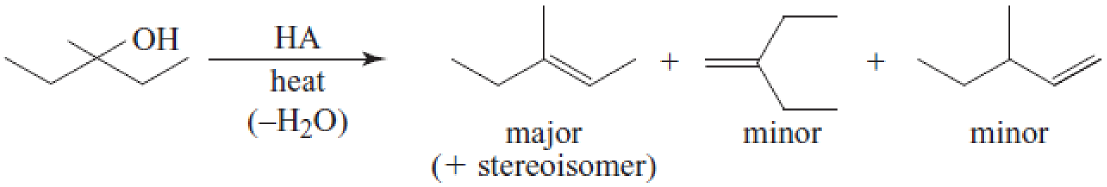
7.40

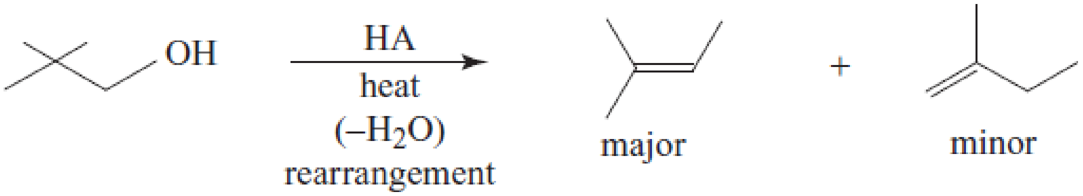
$$\underset{3^\circ}{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_2CH_3} > \underset{2^\circ}{CH_3\underset{\underset{OH}{|}}{C}H\overset{\overset{CH_3}{|}}{C}HCH_3} > \underset{1^\circ}{CH_3CH_2CH_2CH_2CH_2OH}$$

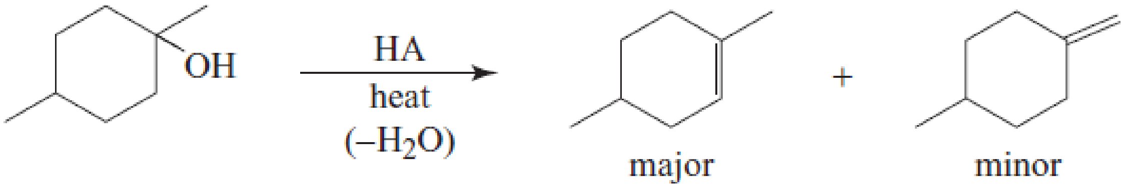
7.41

(a) 

(b) 

(c) 

(d) 

(e) 

7.42

The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

7.43

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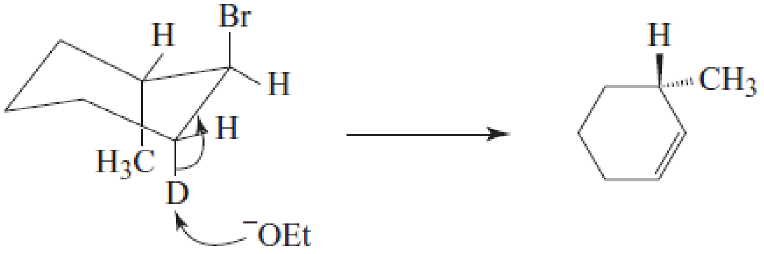
Only the deuterium atom can assume the anti coplanar orientation necessary for an E2 reaction to occur.



7.44

(a) Three

(b) One

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<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (c) It is syn addition to cis alkene and the product would have a plane of symmetry.

2. (a) The Lindlar's catalyst would give a cis product which would then undergo a syn addition of D.

3. **(c)** It is E2 reaction because the reaction involves base with heating.

4. **(b)** The reaction requires Birch reduction (Na/NH_3).

5. **(b)** One mole HBr is eliminated by KOH and one mole by $NaNH_2$.

6. **(a)** E2 elimination is anti-elimination and gives more stable alkene.

7. **(d)** Apply CIP rule.

8. **(d)** $NaNH_2$ will act as base and deprotonate terminal alkyne, which will then give SN2 with alkyl bromide.

9. **(b)** The product P would be according to bulkier base elimination Hoffman product (E2) while the second reaction is E1 dehydration.

10. **(d)** It is unimolecular elimination.

11. **(b)** It is E1 reaction along with rearrangement.

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12. **(d)** Apply CIP rule and IUPAC naming rule.

13. **(b)** It is Pinacole-Pinacolone rearrangement.

14. **(d)** Most stable due to maximum hyperconjugation (most α H).

15. **(b)** No Cl is eliminated in reaction 1 while in the reaction 2, all 6 Cl atoms are eliminated (SN2 with Cl replaced by I and followed by E2 with elimination of ICl.)

16. **(c)** It is E1 reaction, most stable alkene will be formed.

17. **(c)** It is E2 reaction.

18. **(b)** Both are E2 reaction, first is Hoffman product while second is Saytzeff product.

19. **(b)** Rearrangement takes place only in b as more stable carbocation is formed upon hydride shift.

20. **(d)**

21. **(b)** It is dehydration reaction.

22. **(a)** Rearrangement of carbocation along with ring expansion.

23. **(c)** Here x=3, y=2. In x, one addition mole of $NaNH_2$ is used for terminal alkyne.

24. **(b)** For E2 reaction, the groups must be anti and in same plane.

25. **(a)** First reaction is elimination (E2), second reaction is Markovnikov Addition and the third reaction is substitution (SN2).

26. **(b)** It is E2 anti-elimination, only one mole of KOH is consumed.

27. **(c)** It would not give substitution as it is acid base reaction.

28. **(a)** Based on stability of carbocation.

29. **(c)** E2 is anti-elimination.

<H2> Multiple Correct Choice Type

1. **(a),(c)** Apply CIP rule.

<H2> Linked Comprehension Type

1. **(d)** High temperature for elimination and distillation to shift the equilibrium in forward direction by removing water.

2. **(d)** P is 2-methylbutene with 9 α H while Q is 1,2-dimethylpentene with 10 α H.

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3. **(a)** It is E1 reaction, stability of carbocation is the determining factor.

4. **(b)** Both O and C have partial positive charge.

<H2> Integer Type

1. (6). The α H atoms are the H atoms attached to the carbons adjacent to the benzene ring.

2. (19) A is 1-methylcyclohexene with 7 α H while B is 2,3-dimethylbut-2-ene with 12 α H.

3. **(5)** The H atom eliminated alongside Br may be from the left C, right C or the bottom carbon. The alkene formed in first case won't have any stereoisomer while the other two cases would have two stereoisomers (cis and trans) each.

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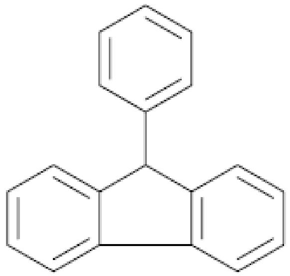
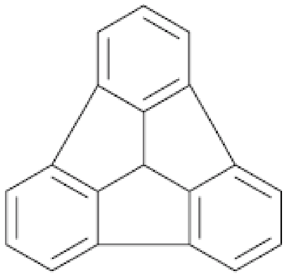
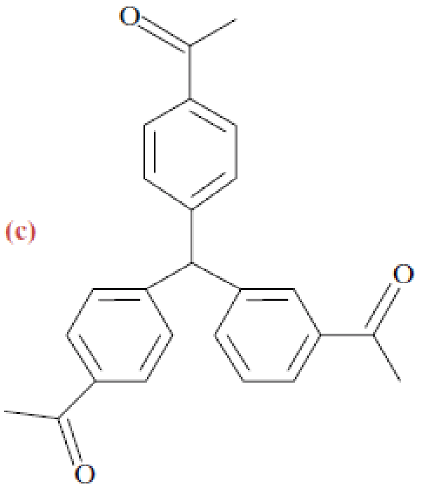
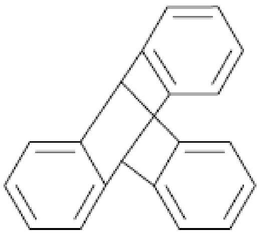
Matrix Match Type

1. Column I Compound	Column II Index of Hydrogen Deficiency
(a) 	(p) 11
(b) 	(q) 12
(c) 	(r) 13
(d) 	(s) 14
	(t) 15

EY

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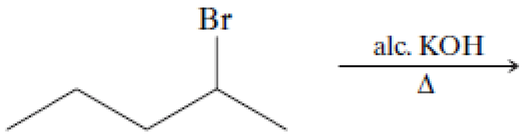
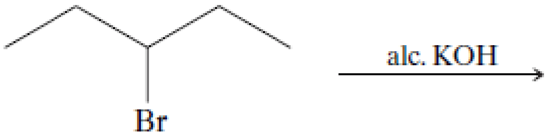
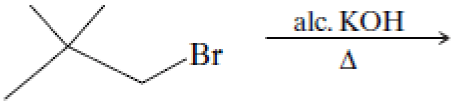
Solution

(a)→(r); (b)→(t); (c)→(t); (d)→(s)

Index of hydrogen deficiency is the sum of number of rings and the number of pi bonds.

2. Column I E2 reaction (elimination bimolecular)	Column II No. of possible products, (including stereoisomerism)
(a) 	(p) 0
(b) 	(q) 1
(c)	(r) 2
(d) 	(s) 3

Solution

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(a)→s; (b)→r; (c)→q; (d)→ p

Products of A are pent-2-ene with cis and trans forms and pent-1-ene.

Product of B is pent-2-ene with cis ad trans forms.

Product of C is but-1-ene.

In D, elimination is not possible as no α H is present.

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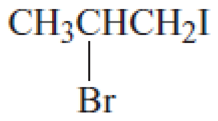
Chapter 8: Alkenes and Alkynes II: Addition Reactions

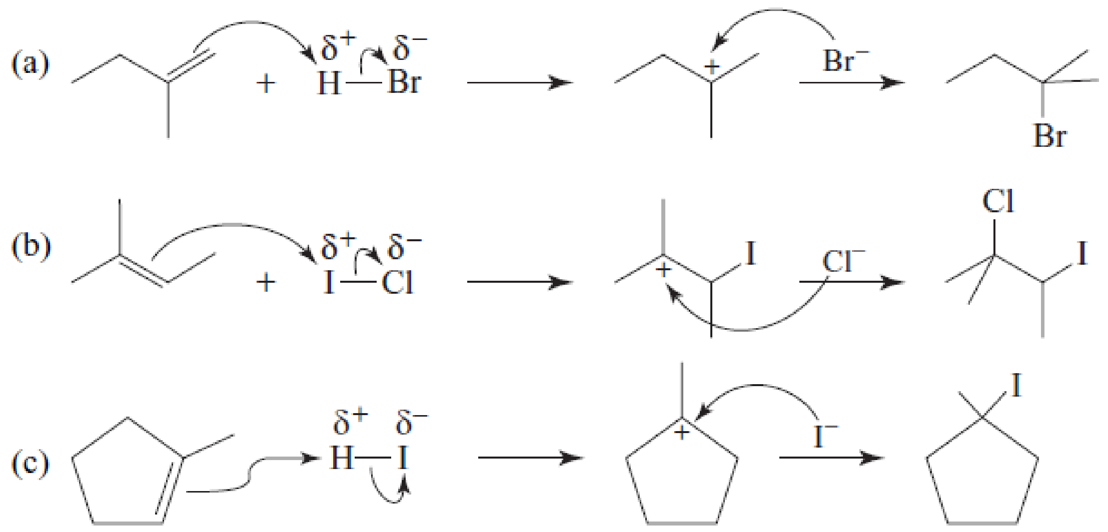
Practice Problems

8.1



2-Bromo-1-iodopropane

8.2



8.3

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow[\text{heat}]{H_2O} CH_3CH_2OH + H_2SO_4$$

8.4

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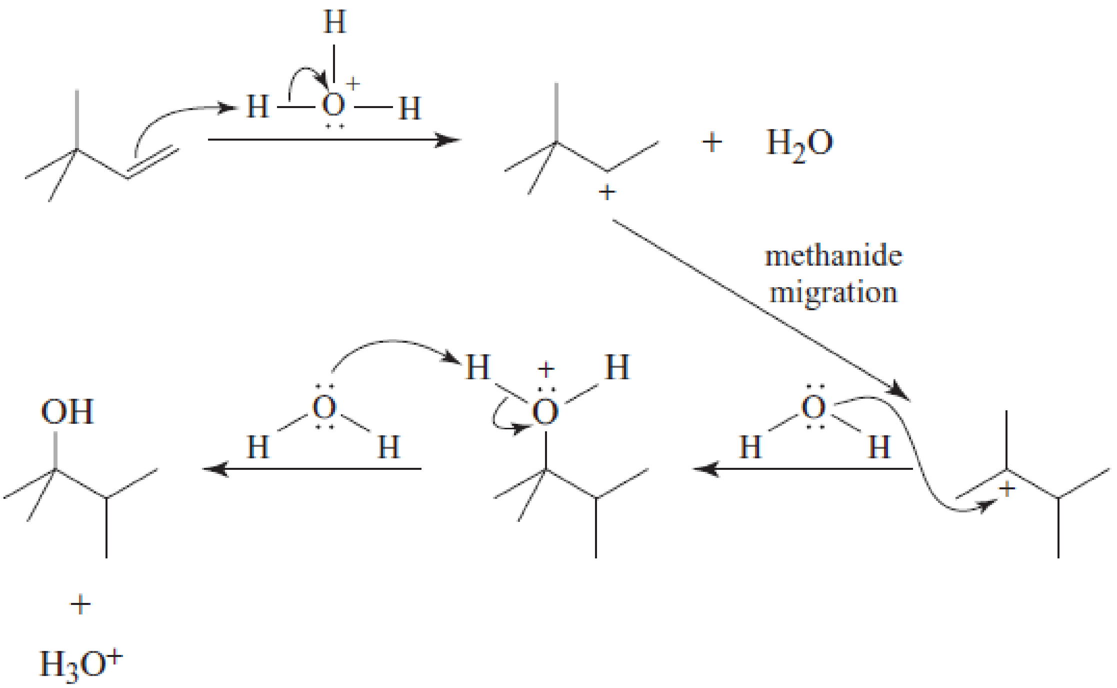

8.5

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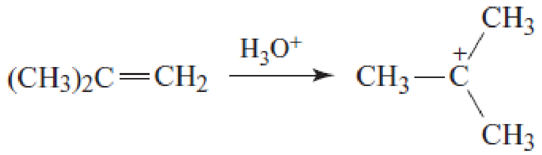
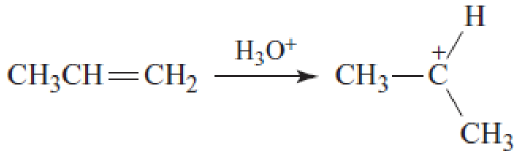
The order reflects the relative ease with which these alkenes accept a proton and form a carbocation. $(CH_3)_2C{=}CH_2$ reacts faster because it leads to a tertiary cation,



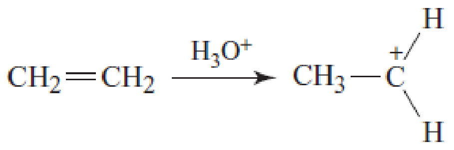
3° Carbocation

$CH_3CH{=}CH_2$ leads to a secondary cation,



2° Carbocation

and $CH_2{=}CH_2$ reacts most slowly because it leads to a primary carbocation.

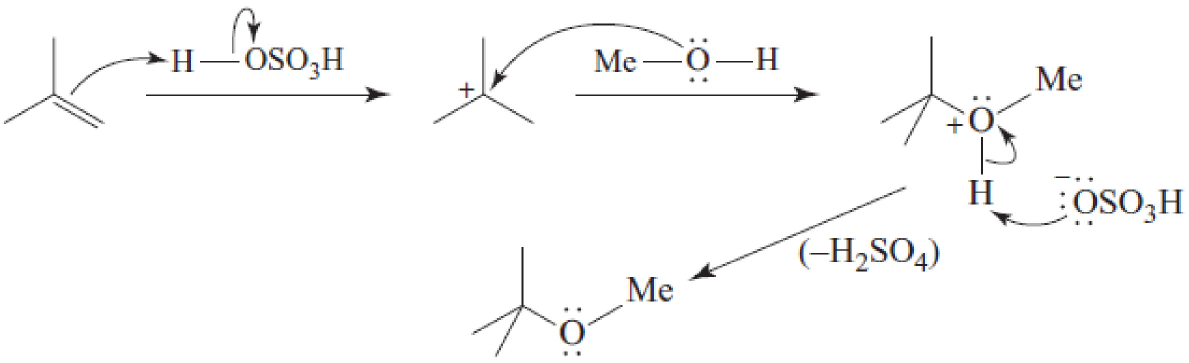


1° Carbocation

Recall that formation of the carbocation is the rate-determining step in acid-catalyzed hydration and that the order of stabilities of carbocations is the following:

$$3° > 2° > 1° > {}^{+}CH_3$$

8.6



8.7

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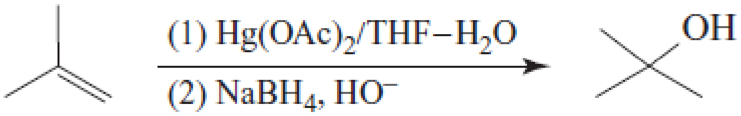
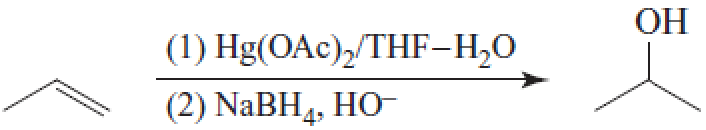
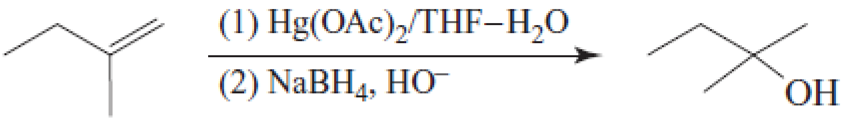
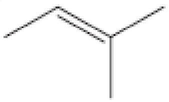
(a) 

(b) 

(c) 

( can also be used.)

8.8

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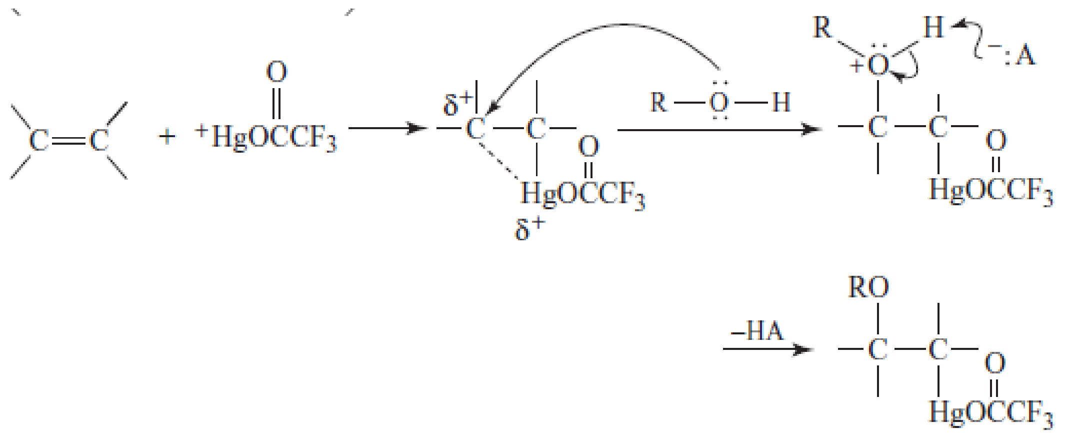
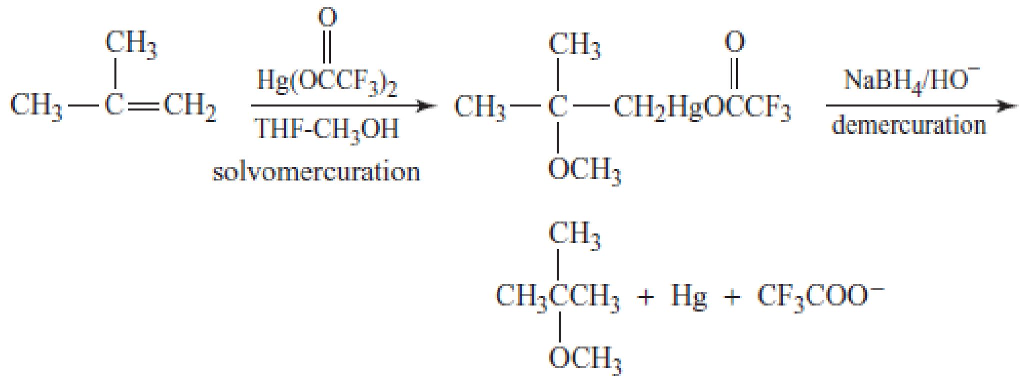
(a) 

(b) 

(c) The electron-withdrawing fluorine atoms in mercuric trifluoroacetate enhance the electrophilicity of the cation. Experiments have demonstrated that for the preparation of tertiary alcohols in satisfactory yields, the trifluoroacetate must be used rather than the acetate.

8.9

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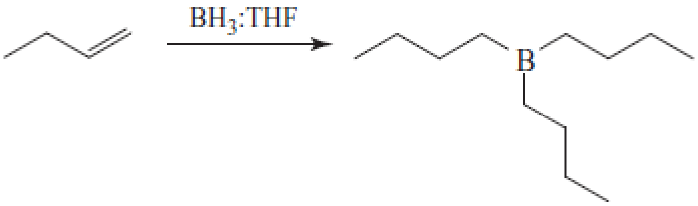
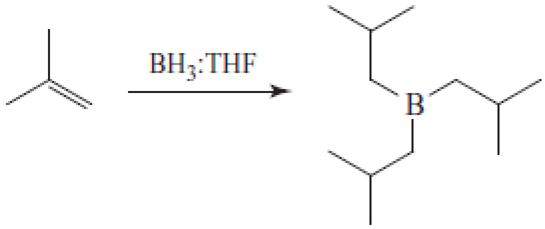
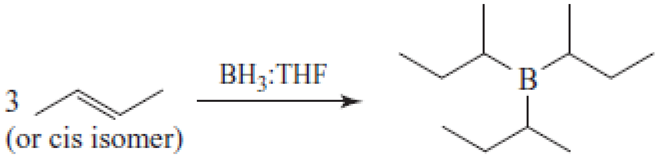
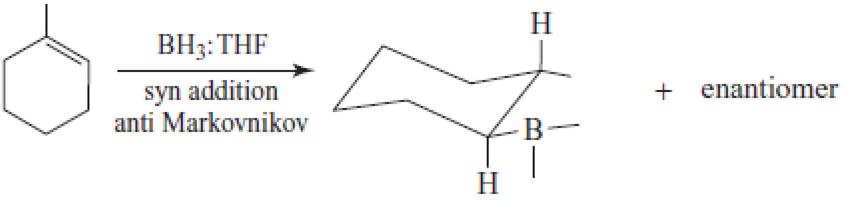
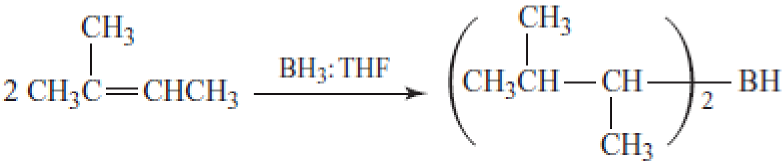
(a) 3 

(b) 3 

(c) 3 

(d) 3 

8.10



Disiamylborane

8.11

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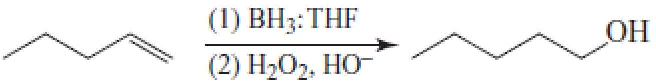
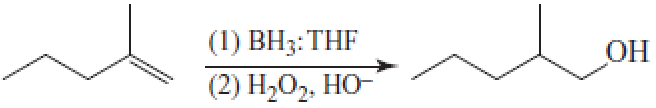
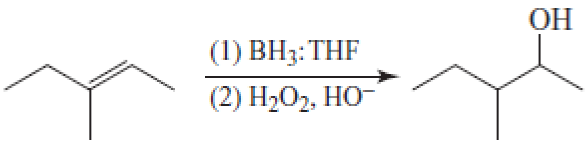
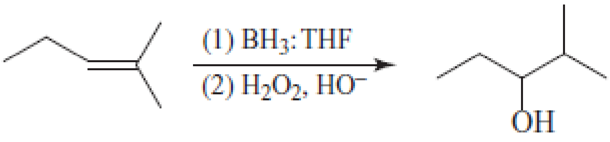
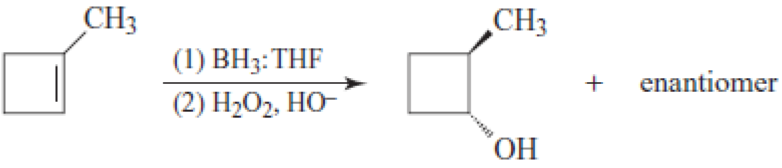
(a) 

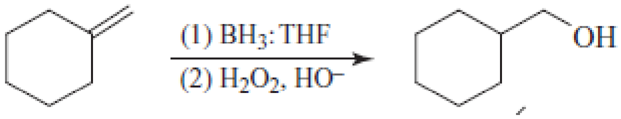
(b) 

(c) 

[or (*Z*) isomer]

(d) 

(e) 

(f) 

8.12

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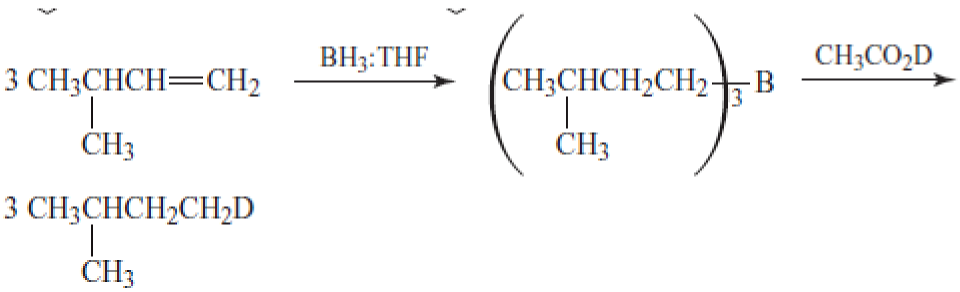
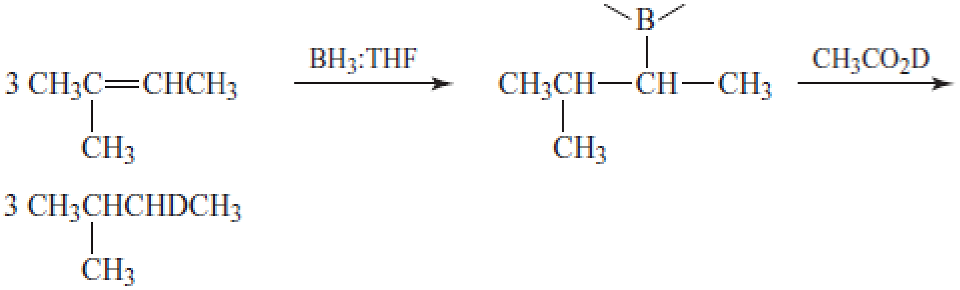
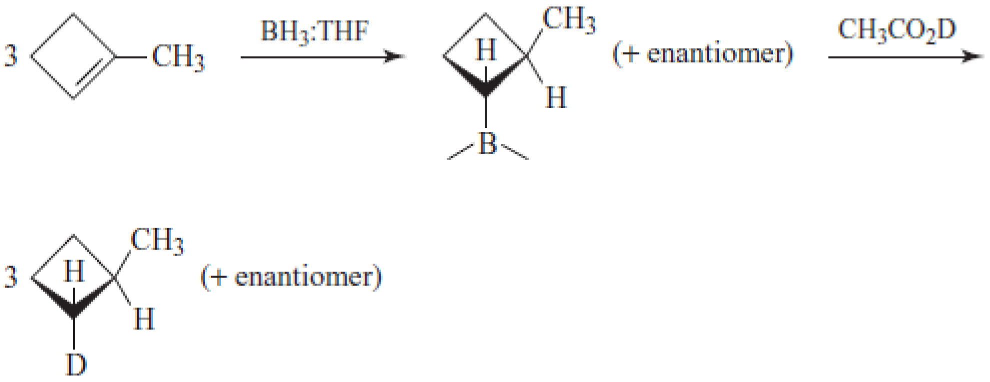
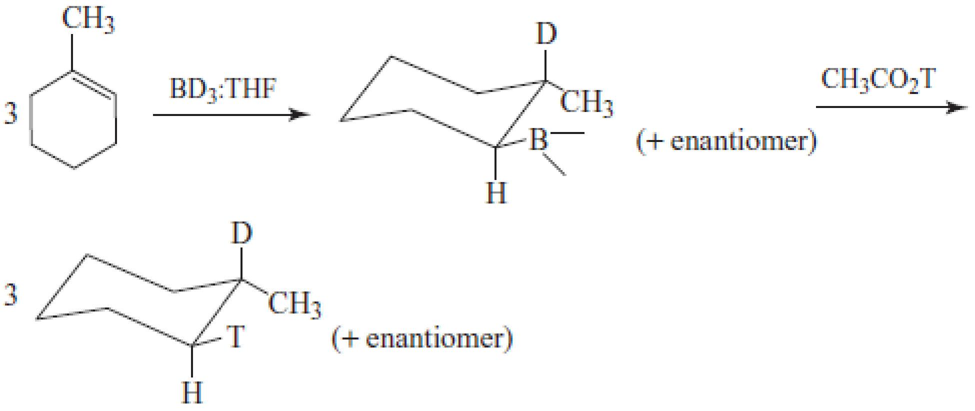
(a) 

(b) 

(c) 

(d) 

8.13

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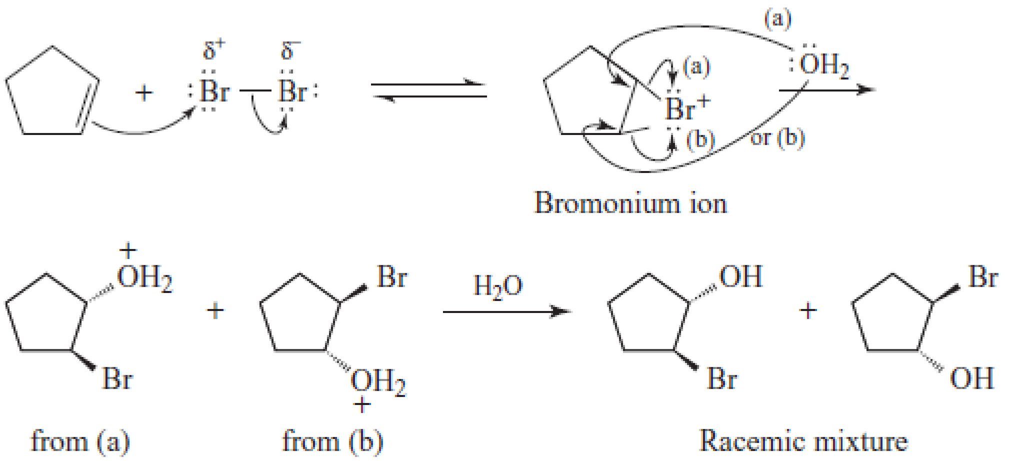
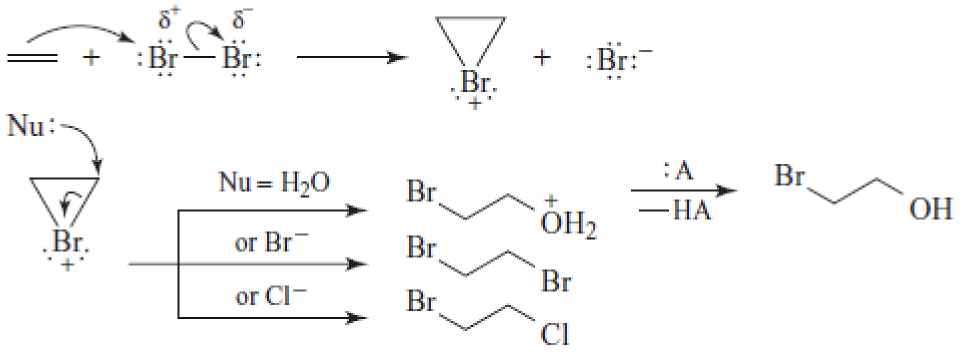


Because paths (a) and (b) occur at equal rates, these enantiomers are formed at equal rates and in equal amounts.

8.14



8.15

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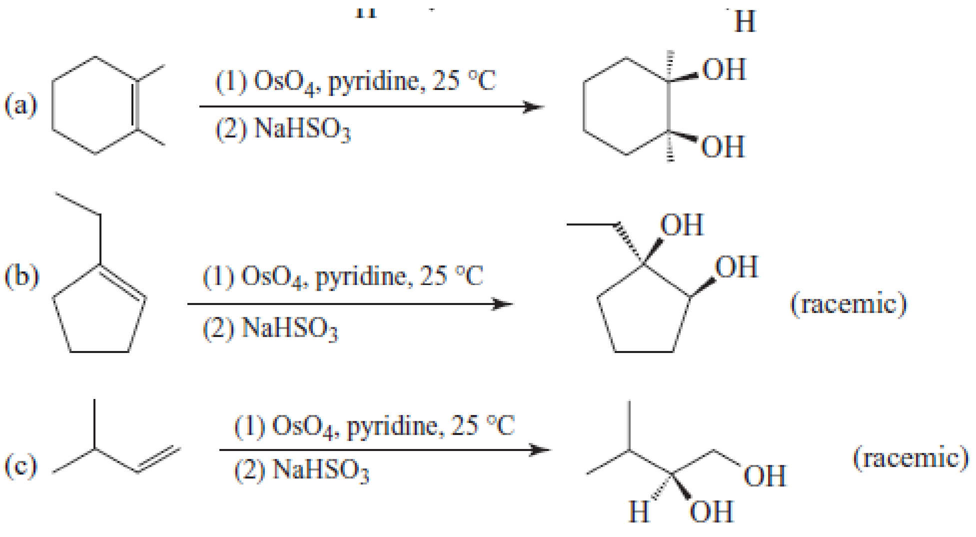
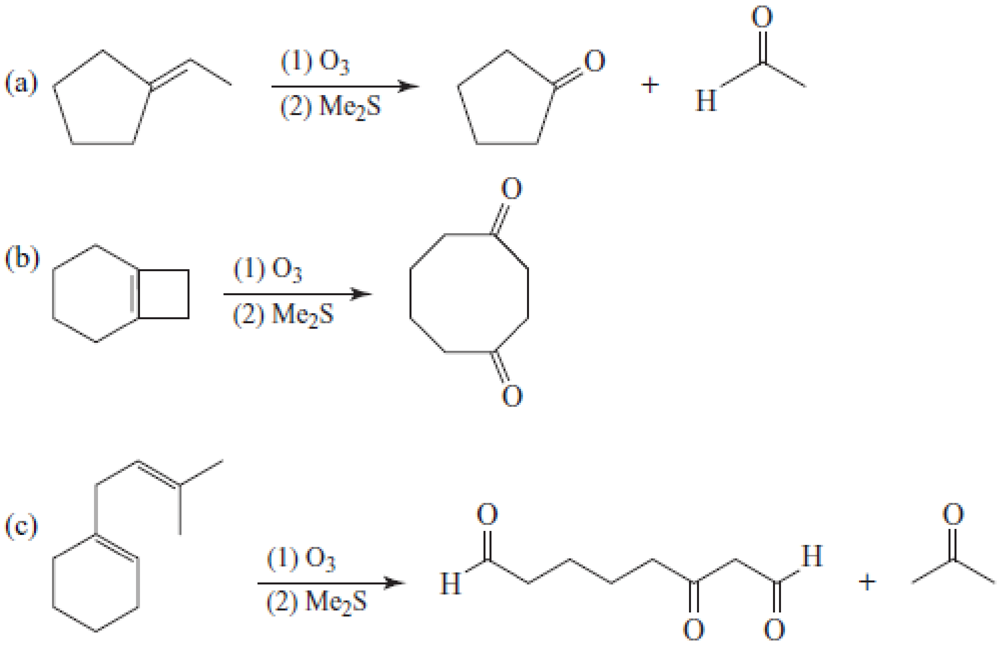


8.16



8.17

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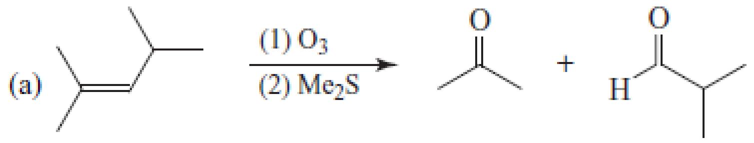
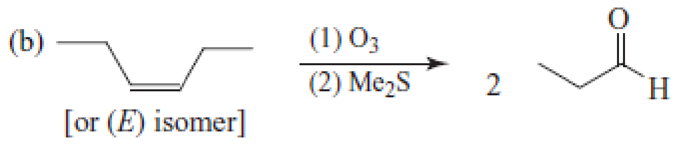
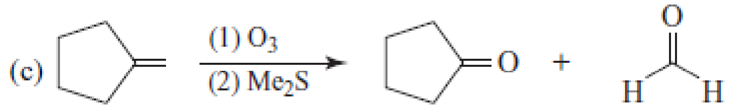
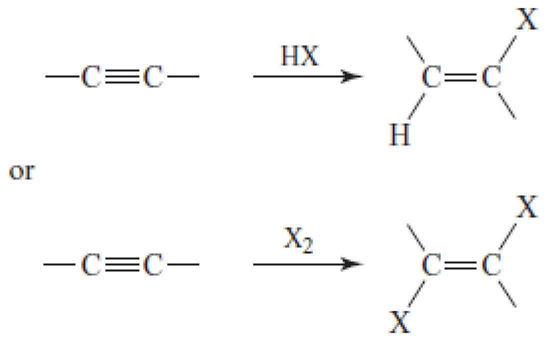






8.18

Ordinary alkenes *are* more reactive toward electrophilic reagents than alkynes. But the alkenes obtained from the addition of an electrophilic reagent to an alkyne have at least one electronegative atom (Cl, Br, etc.) attached to a carbon atom of the double bond.



These alkenes are less reactive than alkynes toward electrophilic addition because the electronegative group makes the double bond "electron poor."

8.19

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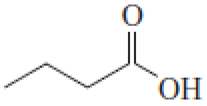
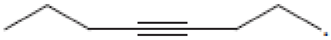
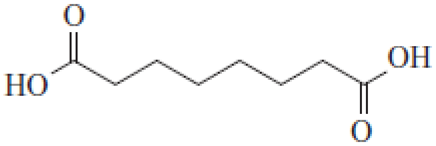
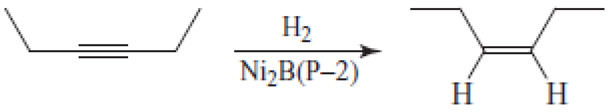
The molecular formula and the formation of octane from **A** and **B** indicate that both compounds are unbranched octynes. Since **A** yields only  on ozonolysis, **A** must be the symmetrical octyne . The IR absorption for **B** shows the presence of a terminal triple bond. Hence **B** is .

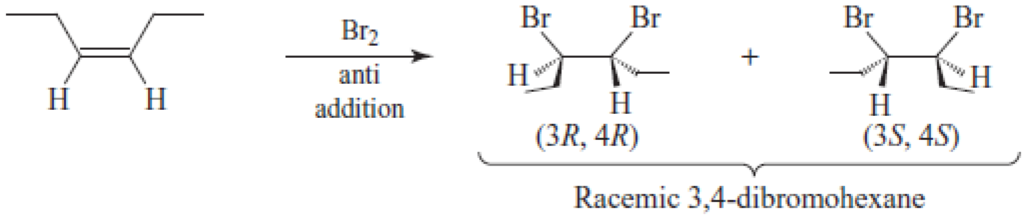
Since **C** (C_8H_{12}) gives  on ozonolysis, **C** must be cyclooctyne. This is supported by the molecular formula of **C** and the fact that it is converted to **D**, C_8H_{16} (cyclooctane), on catalytic hydrogenation.

8.20

By converting the 3-hexyne to *cis*-3-hexene using H_2/Ni_2B (P-2).



Then, addition of bromine to *cis*-3-hexene will yield (3*R*,4*R*), and (3*S*,4*S*)-3,4-dibromohexane as a racemic form.



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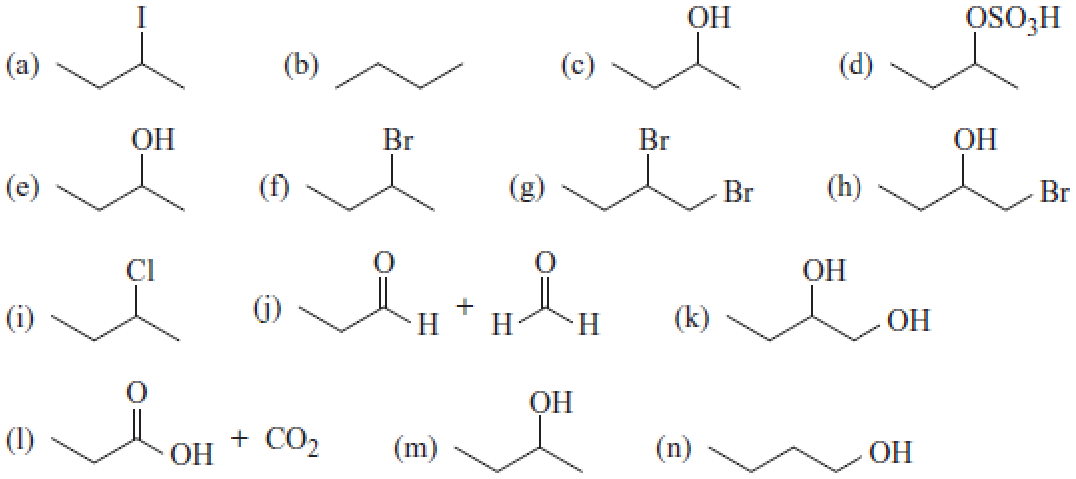
Review Problems

Alkenes and Alkynes Reaction Toolkit

8.21

The answers to all parts except (b), (j), (l), and (n) are formed as racemic mixtures.



8.22

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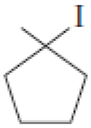
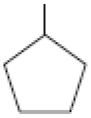
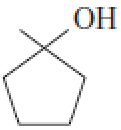
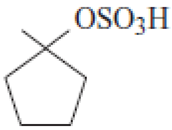
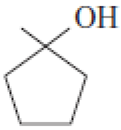
The answers to (g), (h), (k), and (n) are formed as racemic mixtures.

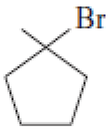
(a) 

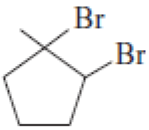
(b) 

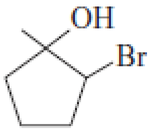
(c) 

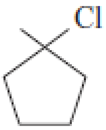
(d) 

(e) 

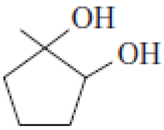
(f) 

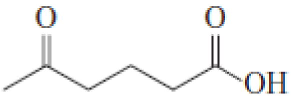
(g) 

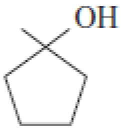
(h) 

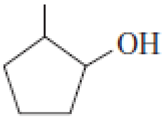
(i) 

(j)

(k) 

(l) 

(m) 

(n) 

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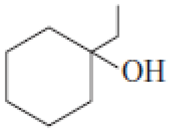
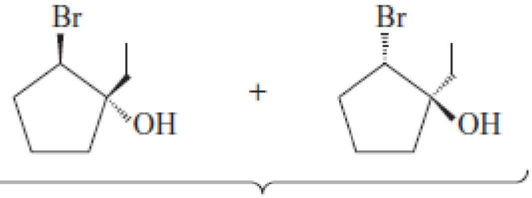
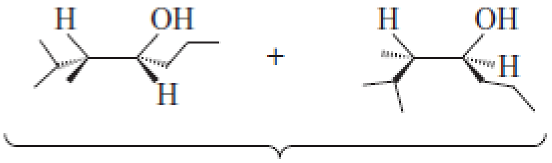
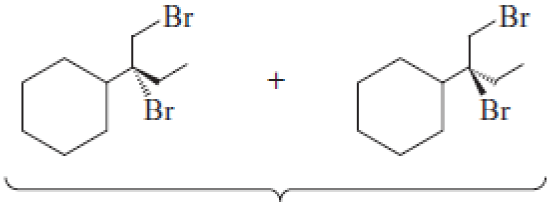
(a) 

(b) 

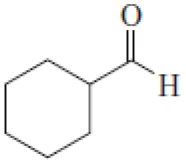
enantiomers

(c) 

enantiomers

(d) 

enantiomers

(e) 2 

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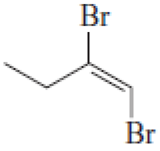
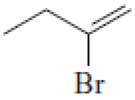
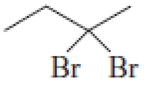
8.24

(a) 

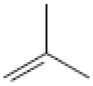
(b) 

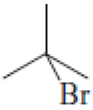
(c) 

(d)

(e)

(f)

(g) and  [An E2 reaction would take place

when $^{-}Na^{+}$ is treated with ]

8.25

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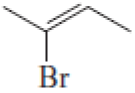
(a) 

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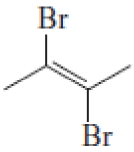
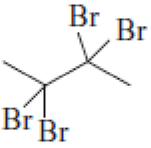
(c) 

(d) 

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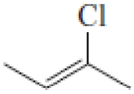
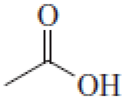
(f) 

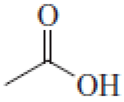
(g)

(h)

(i)

(j) 

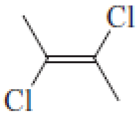
(2 molar equivalents)

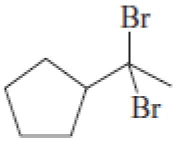
(k) 

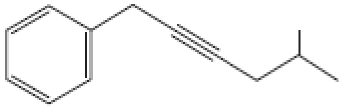
(2 molar equivalents)

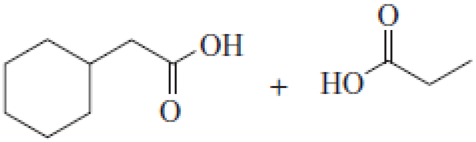
(l) No reaction

8.26

(a) 

(b) 

(c) 

(d) 

8.27

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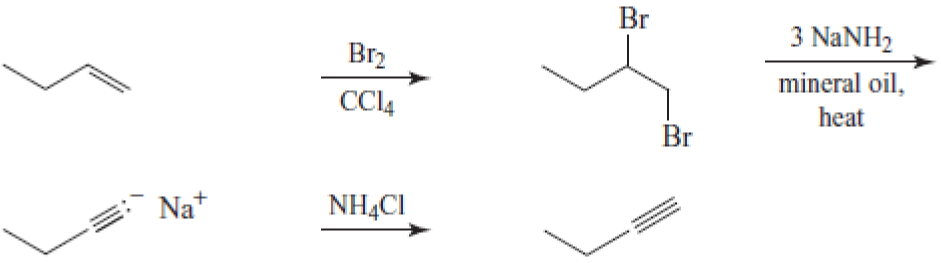
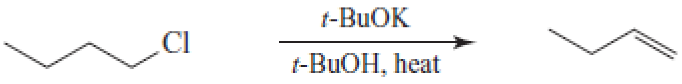
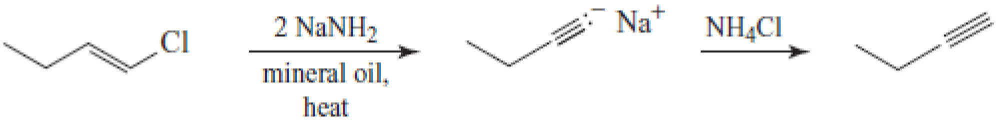
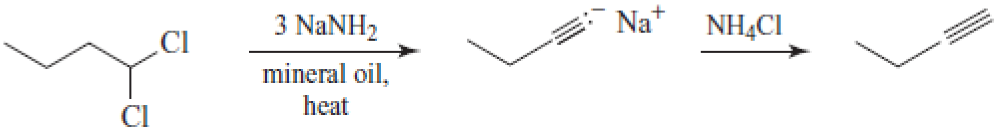
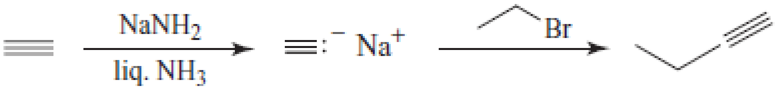
(a) 

(b) 

Then as in (a)

(c) 

(d) 

(e) 

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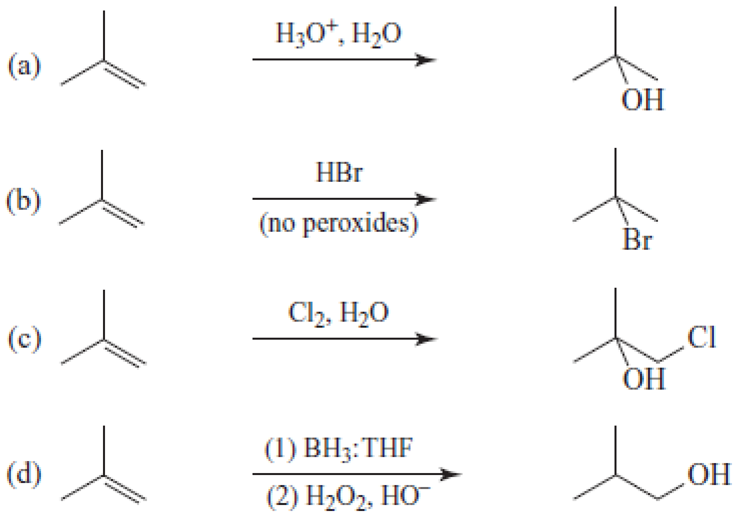
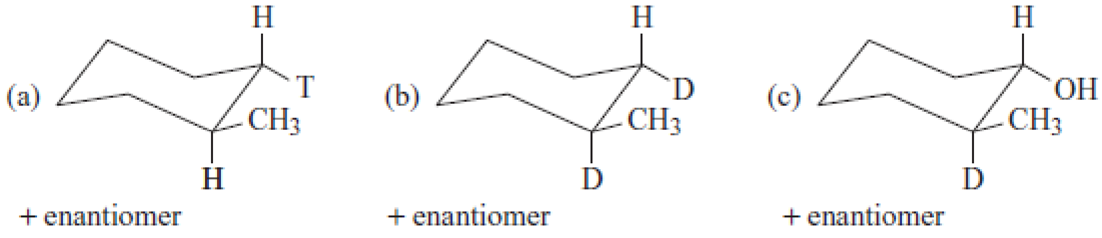


Mechanisms

8.29



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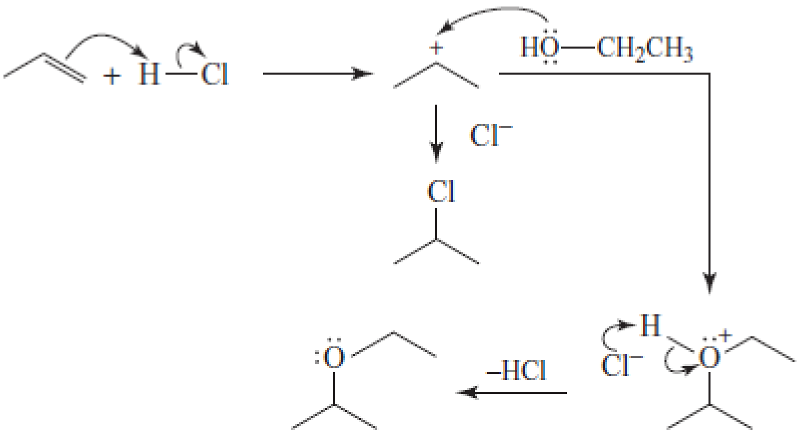
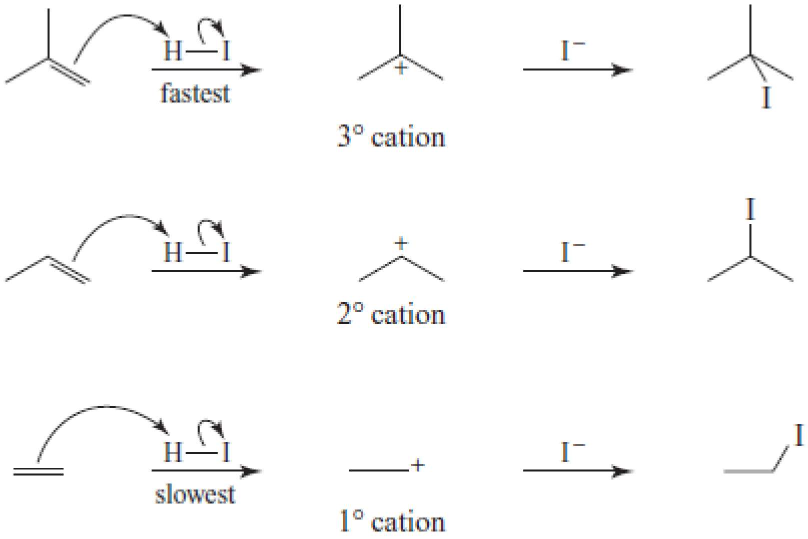


8.31

The rate-determining step in each reaction is the formation of a carbocation when the alkene accepts a proton from HI. When 2-methylpropene reacts, it forms a 3° carbocation (the most stable); therefore, it reacts fastest. When ethene reacts, it forms a 1° carbocation (the least stable); therefore, it reacts the slowest.



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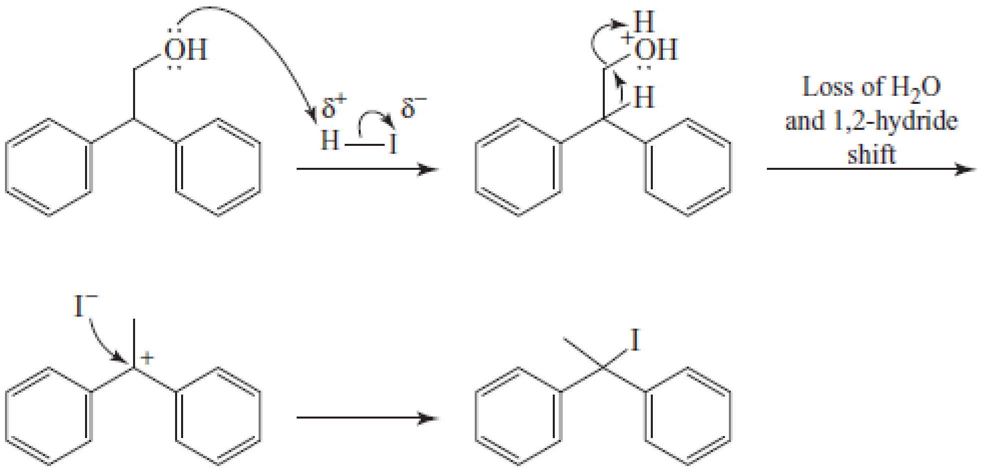

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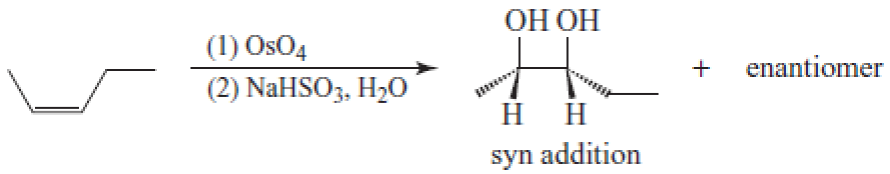
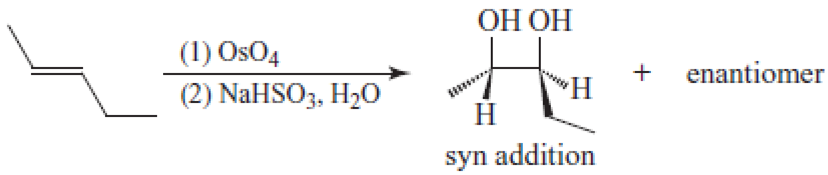
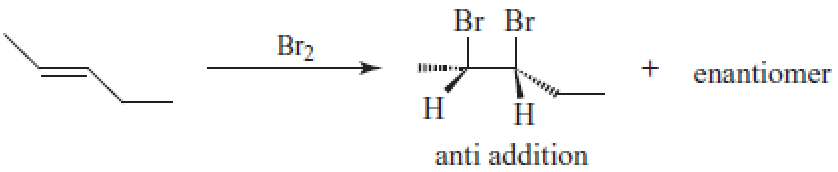
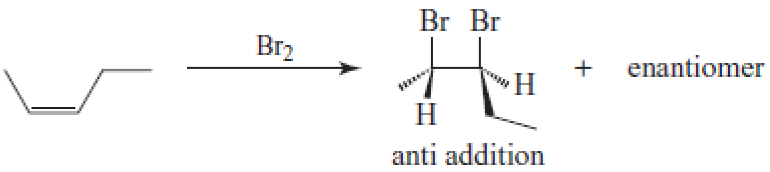
(a) 

(b) 

(c) 

(d) 

8.34

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(a) (2*S*, 3*R*)- [the enantiomer is (2*R*, 3*S*)-]

(b) (2*S*, 3*S*)- [the enantiomer is (2*R*, 3*R*)-]

(c) (2*S*, 3*R*)- [the enantiomer is (2*R*, 3*S*)-]

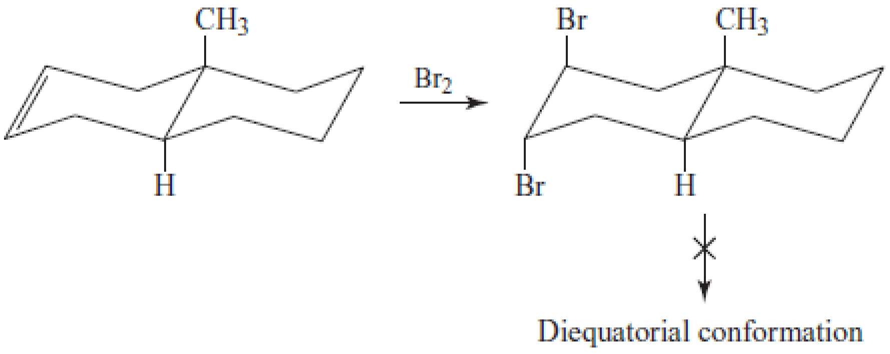
(d) (2*S*, 3*S*)- [the enantiomer is (2*R*, 3*R*)-]

8.35

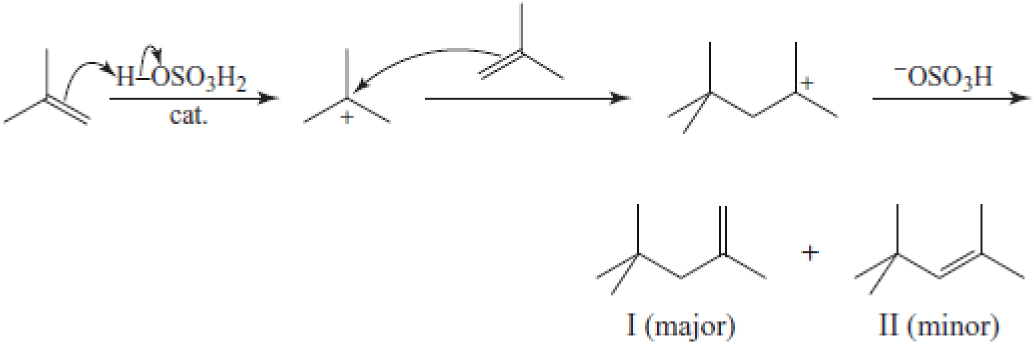
Because of the electron-withdrawing nature of chlorine, the electron density at the double bond is greatly reduced and attack by the electrophilic bromine does not occur.

8.36

The bicyclic compound is a *trans*-decalin derivative. The fused nonhalogenated ring prevents the ring flip of the bromine-substituted ring necessary to give equatorial bromines.



8.37



Though II is the product predicted by application of the Zaitsev rule, it actually is less stable than I due to crowding about the double bond. Hence I is the major product (by about a 4:1 ratio).

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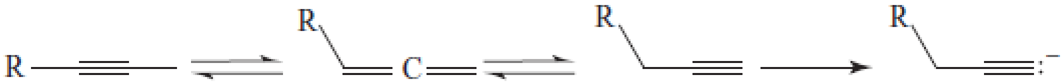
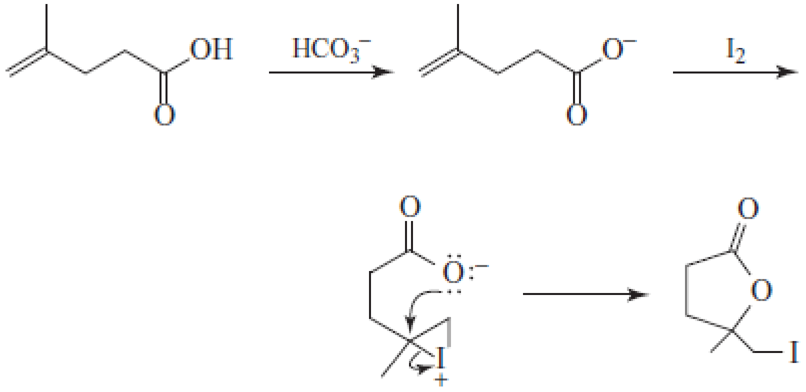
8.38

The terminal alkyne component of the equilibrium established in base is converted to a salt by $NaNH_2$, effectively shifting the equilibrium completely to the right.

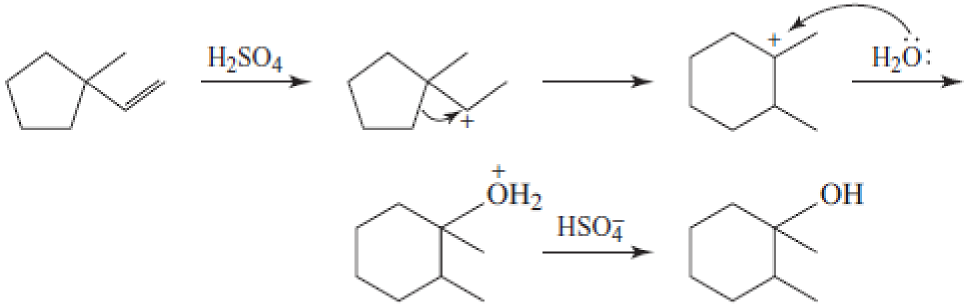


NaOH is too weak a base to form a salt with the terminal alkyne. Of the equilibrium components with NaOH, the internal alkyne is favored since it is the most stable of these structures. Very small amounts of the allene and the terminal alkyne are formed.

8.39



8.40



8.41

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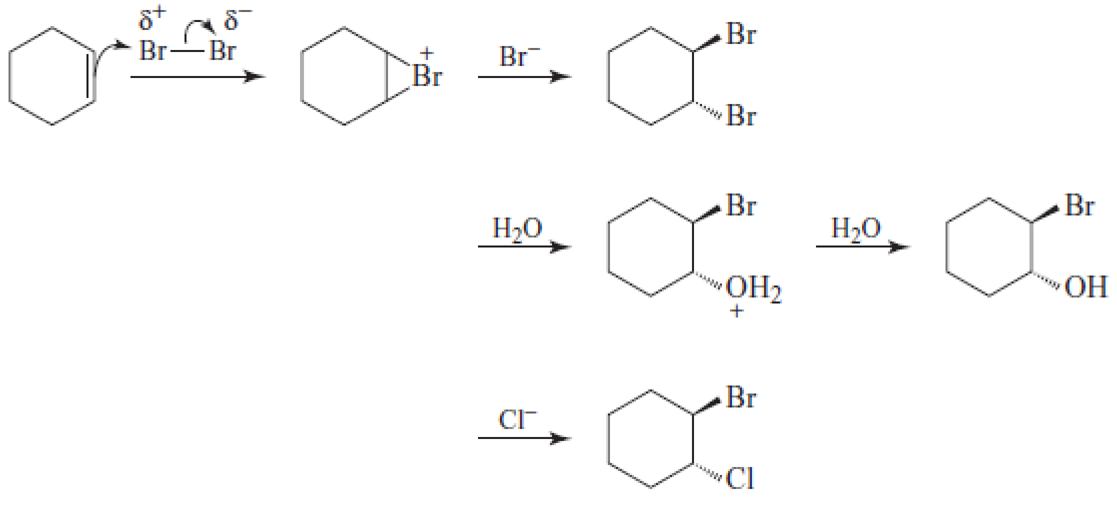

Enantiomers of each also formed.

Structure Elucidation

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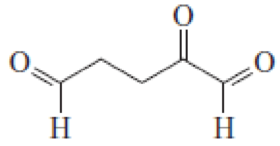
8.42

(a) $C_{10}H_{22}$ (saturated alkane)
$\underline{C_{10}H_{16}}$ (formula of myrcene)
$H_6 = 3$ pairs of hydrogen atoms
Index of hydrogen deficiency (IHD) = 3

(b) Myrcene contains no rings because complete hydrogenation gives $C_{10}H_{22}$, which corresponds to an alkane.

(c) That myrcene absorbs three molar equivalents of H_2 on hydrogenation indicates that it contains three double bonds.

(d) 

(e) Three structures are possible; however, only one gives 2,6-dimethyloctane on complete hydrogenation. Myrcene is therefore

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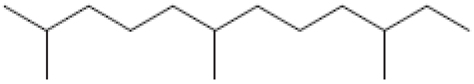
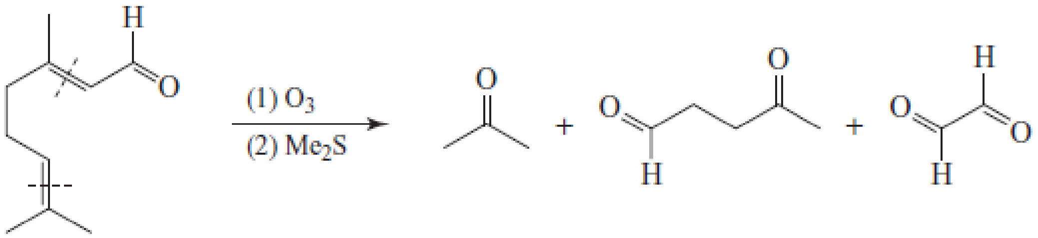
8.43

(a)  (b) Four

2,6,10-Trimethyldodecane

8.44



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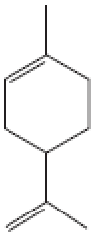

Limonene

General Problems

8.46

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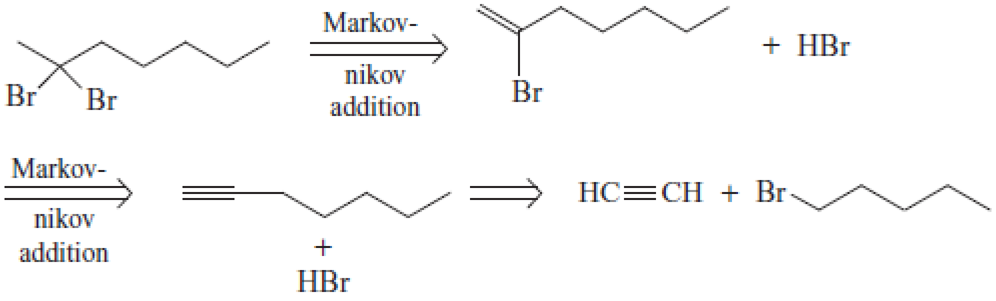
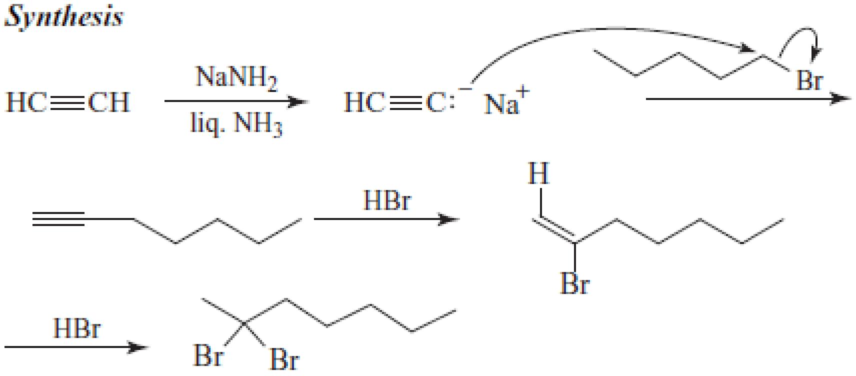
Retrosynthetic analysis



Synthesis



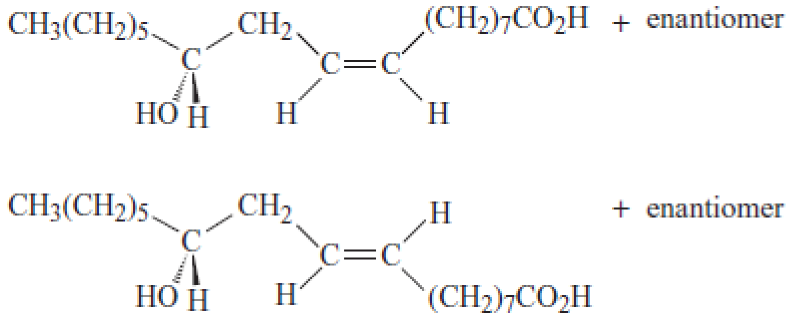
8.47

Syn hydrogenation of the triple bond is required. So use H_2 and Ni_2B(P-2) or H_2 and Lindlar's catalyst.

8.48

(a) Four

(b)



8.49

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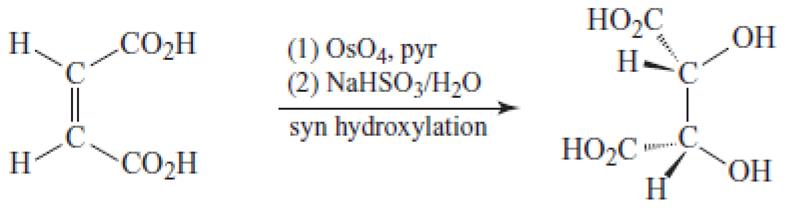
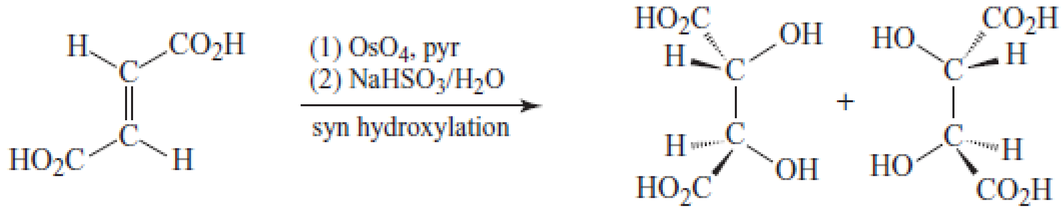
Hydroxylations by OsO_4 are syn hydroxylations (cf. Section 8.16). Thus, maleic acid must be the cis-dicarboxylic acid:



Maleic acid

meso-Tartaric acid

Fumaric acid must be the trans-dicarboxylic acid:

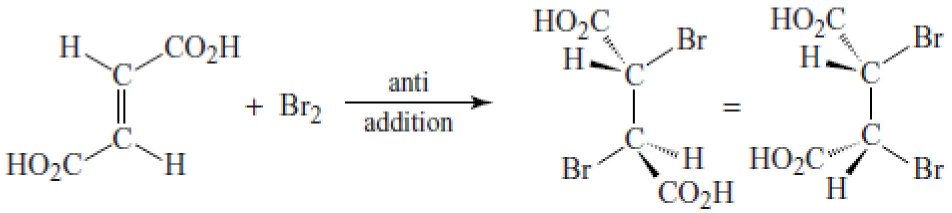


Fumaric acid

(±)-Tartaric acid

8.50

(a) The addition of bromine is an anti addition. Thus, fumaric acid yields a meso compound.



A meso compound

(b) Maleic acid adds bromine to yield a racemic form.

8.51

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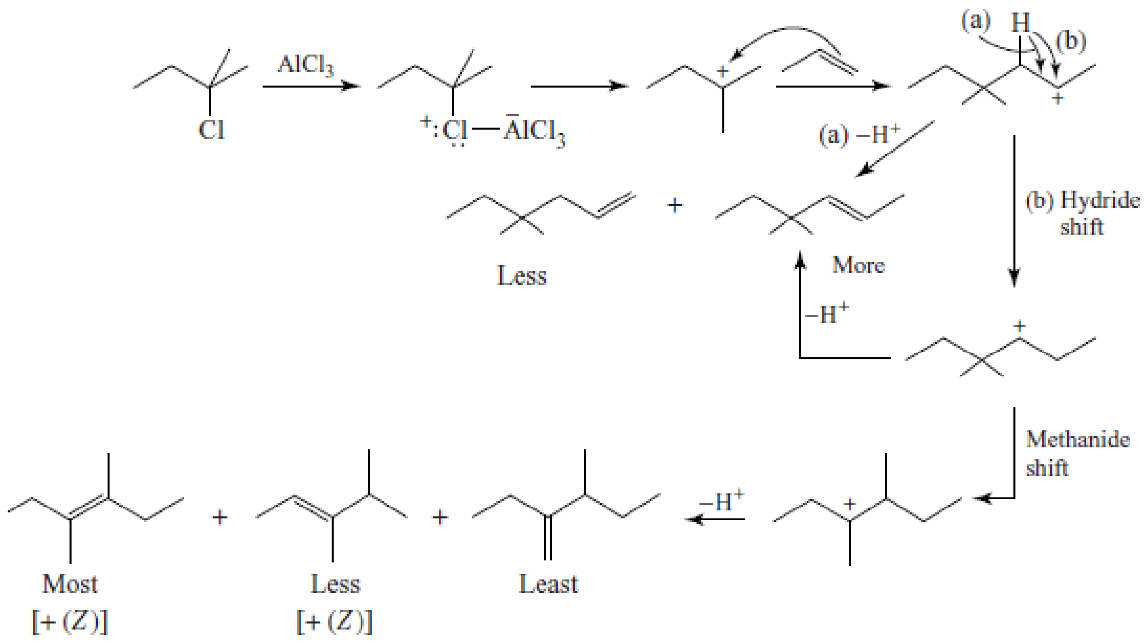

Each carbocation can combine with chloride ion to form a racemic alkyl chloride.

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8.52

The catalytic hydrogenation involves syn addition of hydrogen to the predominantly less hindered face of the cyclic system (the face lacking 1,3-diaxial interactions when the molecule is adsorbed on the catalyst surface). This leads to I, even though II is the more stable of the two isomers since both methyl groups are equatorial in II.

8.53

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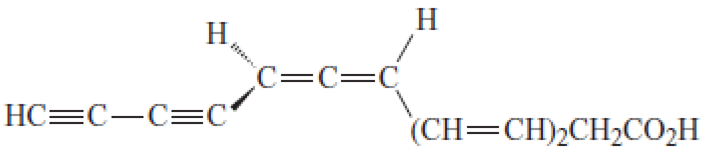

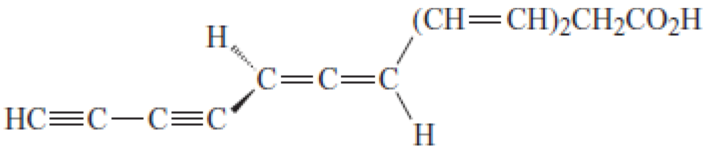

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. **(c)** It is Markovnikov addition.

2. (a) In Ozonolysis, replace C=C with C=O.

3. (a) Markovnikov addition of OH followed by tautomerism, Kucherov reaction.

4. (a) TCP will be as per stability of carbocation intermediate while the TCP will be as per the most stable alkene product.

5. (d) Tollen's test.

6. (b) The left side alkyne would be reduced to cis alkene, thus the product is optically inactive.

7. (b) It will be anti-addition of I (electrophile) and Cl (nucleophile).

8. (b) Addition of Cl^+ in first step and OH^- in second step.

9. (d) Order of rate of reaction is as per stability of carbocation intermediate.

10. (a) Markovnikov addition of OH followed by Tautomerism.

11. (c) In Ozonolysis, replace C=C with C=O.

12. (b) Birch reaction gives trans alkene.

13. (a) Markovnikov addition of Cl^- and NO^+.

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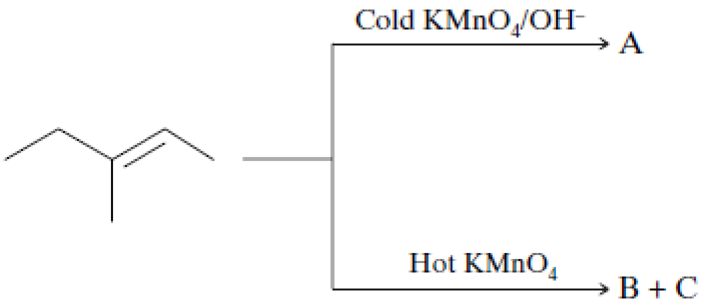
15.



15. (c) First would give addition of OH groups (Baeyer's reagent) while the second reaction would involve oxidation.

16. (a) In Ozonolysis, replace C=C with C=O.

17. (d) Only alkene or alkyne would form ozonide upon ozonolysis.

18. (c) Lindlar's catalyst would reduce the alkyne to cis alkene and thus would result in generation of a chiral carbon.

19. (c) Ehtylene is CH_2=CH_2 which result in an addition reaction with Baeyer's reagent (Cold $KMnO_4$ in basic medium).

20. (c) The Br_2 addition would be anti and would result in an optically active product with two enantiomeric forms.

21. (d) A more stable carbocation should form in single step for hydrogen shift in rearrangement.

22. (c) In c, dehydration could be with proton from the right or left side of OH group.

23. (b) All are markovnikov addition with OH, OCH_3 and OD respectively as nucleophiles.

24. (c) Alkene would result in decolorisation.

25. (d) All are Markovnikov addition of HBr.

<H2> Integer Type

1. (8) The six *sp* C atoms and the two sp^3 C atoms at either end attached to *sp* C, would be collinear.

2. (1)

<H2> Matrix Match Type

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1. a →(p, q); b→(r, s); c→(r, s); d→(p, q)

In option (a): H_2/Pd-$BaSO_4$ (Lindlar's catalyst) gives cis alkene with alkyne while Na/Liq.NH_3 (Birch reduction) gives trans alkene with alkyne.

In option (b): The terminal alkyne will give tollen's test and also release H_2 gas with active metal Na.

In option (c): The terminal alkyne will give tollen's test and also release H_2 gas with active metal Na.

In option (d): H_2/Pd-$BaSO_4$ (Lindlar's catalyst) gives cis alkene with alkyne while Na/Liq.NH_3 (Birch reduction) gives trans alkene with alkyne.

2. a→(r, s, z); b→(p, s, y); c→(p, s, y); d→(q, s, y)

Br_2/CCl_4 would result in anti-addition of the two Br atoms to the alkene.

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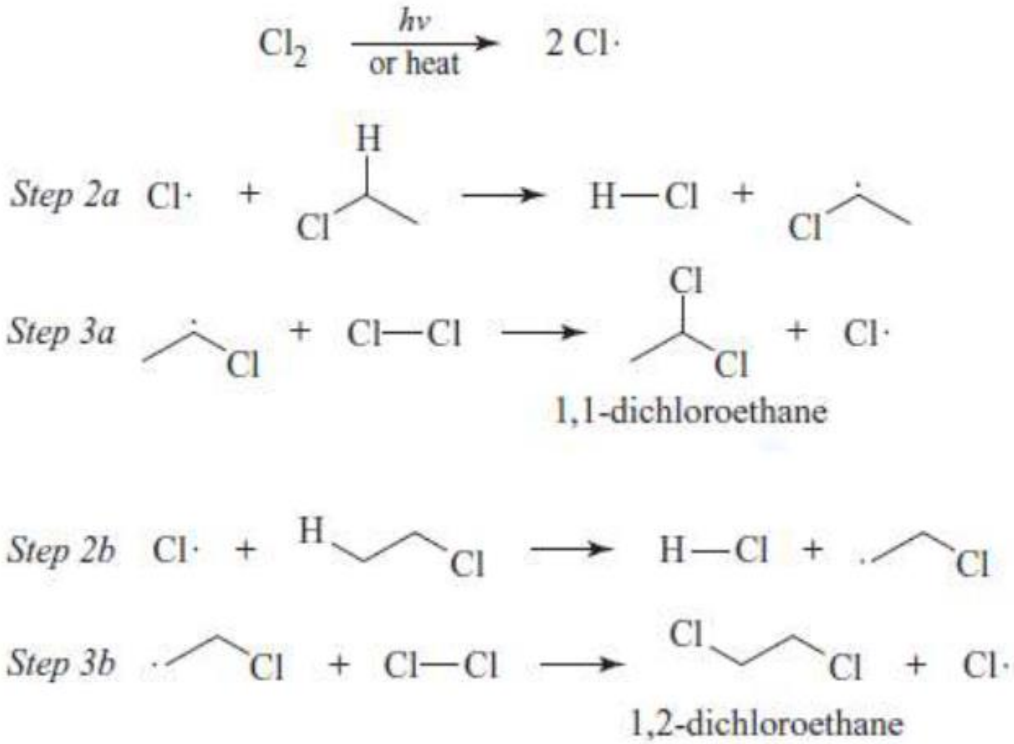
Chapter 9: Radical Reactions

Practice Problems

9.1

3° > 2° > 1° > Methyl

9.2



9.3

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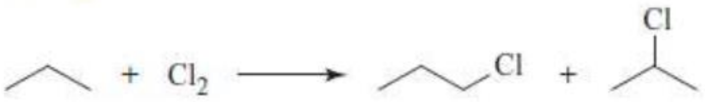
(a) There is a total of eight hydrogen atoms in propane. There are six equivalent 1° hydrogen atoms, replacement of any one of which leads to propyl chloride, and there are two equivalent 2° hydrogen atoms, replacement of any one of which leads to isopropyl chloride.

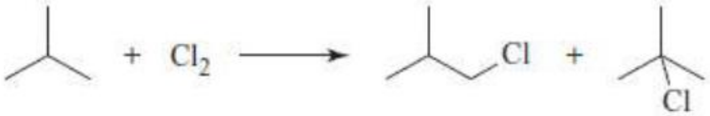


If all the hydrogen atoms were equally reactive, we would expect to obtain 75% propyl chloride and 25% isopropyl chloride:

$$\% \text{ Propyl chloride} = \tfrac{6}{8} \times 100 = 75\%$$

$$\% \text{ Isopropyl chloride} = \tfrac{2}{8} \times 100 = 25\%$$

(b) Reasoning in the same way as in part (a), we would expect 90% isobutyl chloride and 10% *tert*-butyl chloride, if the hydrogen atoms were equally reactive.



$$\% \text{ Isobutyl chloride} = \tfrac{9}{10} \times 100 = 90\%$$

$$\% \textit{ tert}\text{-Butyl chloride} = \tfrac{1}{10} \times 100 = 10\%$$

(c) In the case of propane (see Section 10.6), we actually get more than twice as much isopropyl chloride (55%) than we would expect if the 1° and 2° hydrogen atoms were equally reactive (25%). Clearly, then, 2° hydrogen atoms are more than twice as reactive as 1° hydrogen atoms.

In the case of isobutane, we get almost four times as much *tert*-butyl chloride (37%) as we would get (10%) if the 1° and 3° hydrogen atoms were equally reactive. The order of reactivity of the hydrogens then must be

$$3° > 2° > 1°$$

9.4

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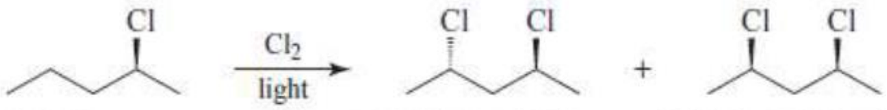
(a) 

(*S*)-2-Chloropentane (2*S*,4*S*)-2,4-Dichloropentane (2*R*,4*S*)-2,4-Dichloropentane

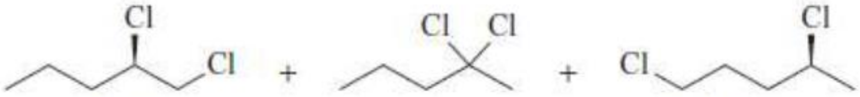
(b) They are diastereomers. (They are stereoisomers, but they are not mirror images of each other.)

(c) No, (2*R*,4*S*)-2,4-dichloropentane is achiral because it is a meso compound. (It has a plane of symmetry passing through C3.)

(d) No, the achiral meso compound would not be optically active.

(e) Yes, by fractional distillation or by gas chromatography. (Diastereomers have different physical properties. Therefore, the two isomers would have different vapor pressures.)

(f and g) In addition to the (2*S*,4*S*)-2,4-dichloropentane and (2*R*,4*S*)-2,4-dichloropentane isomers described previously, we would also get (2*S*,3*S*)-2,3-dichloropentane, (2*S*,3*R*)-2,3-dichloropentane and the following:



(optically active) (optically inactive) (optically active)

9.5

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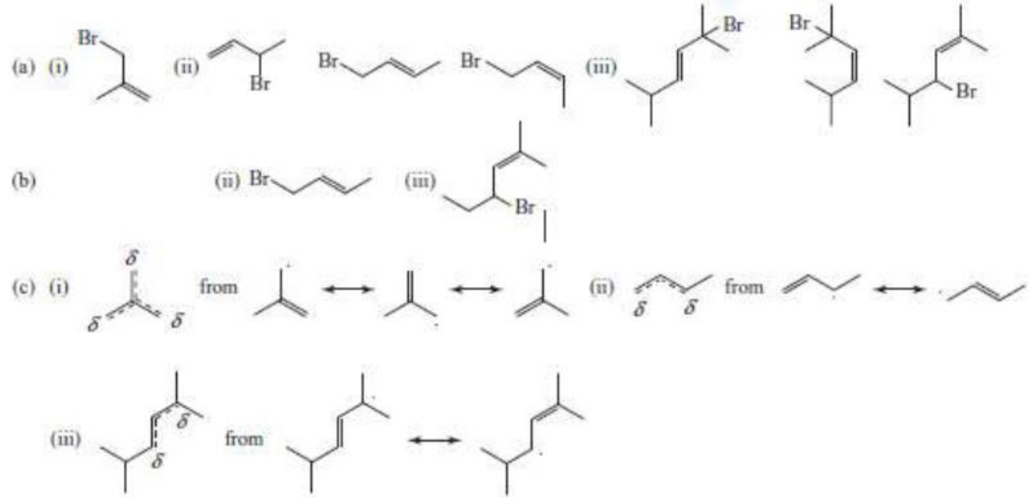
(a) The only fractions that would contain chiral molecules (as enantiomers) would be those containing 1-chloro-2-methylbutane and the two diastereomers of 2-chloro-3-methylbutane. These fractions would not show optical activity, however, because they would contain racemic forms of the enantiomers.

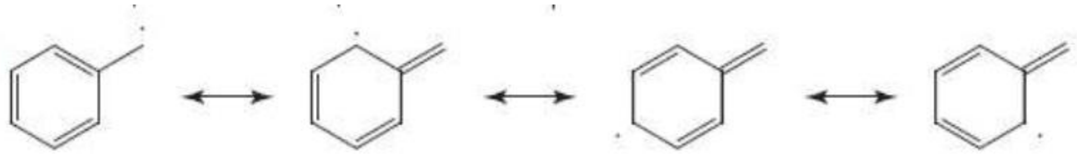
(b) Yes, the fractions containing 1-chloro-2-methylbutane and the two containing the 2-chloro-3-methylbutane diastereomers.

(c) Yes, each fraction from the distillation could be identified on the basis of ^1H NMR spectroscopy. The signals related to the carbons where the chlorine atom is bonded would be sufficient to distinguish them. The protons at C1 of 1-chloro-2-methylbutane would be a doublet due to splitting from the single hydrogen at C2. There would be no proton signal for C2 of 2-chloro-2-methylbutane since there are no hydrogens bonded at C2 in this compound; however there would be a strong singlet for the six hydrogens of the geminal methyl groups. The proton signal at C2 of 2-chloro-3-methylbutane would approximately be a quintet, due to combined splitting from the three hydrogens at C1 and the single hydrogen at C3. The protons at C1 of 1-chloro-3-methylbutane would be a triplet due to splitting by the two hydrogens at C2.

9.6



9.7



9.8

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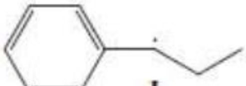
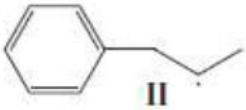
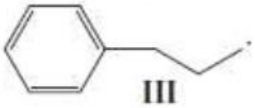


I leads to 1-chloro-1-phenylpropane

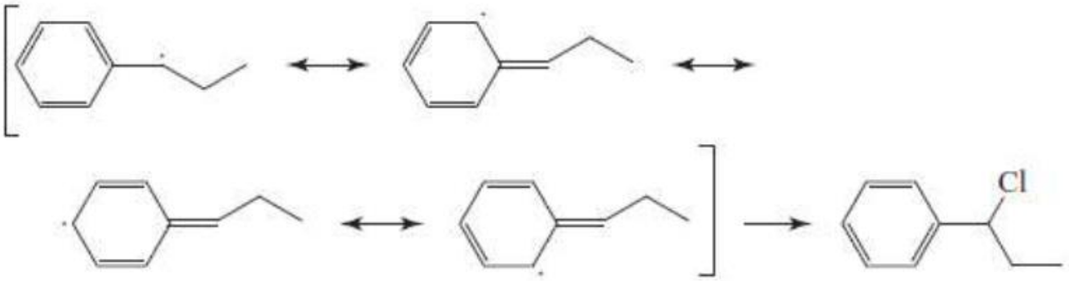


II leads to 2-chloro-1-phenylpropane



III leads to 1-chloro-3-phenylpropane

The major product is 1-chloro-1-phenylpropane because **I** is the most stable radical. It is a benzylic radical and therefore is stabilized by resonance.



9.9

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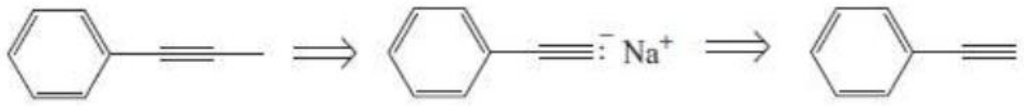
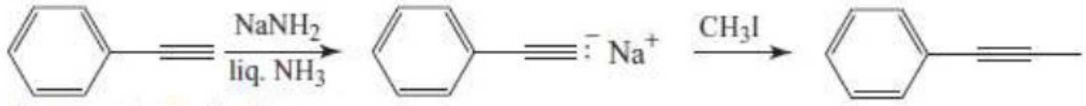
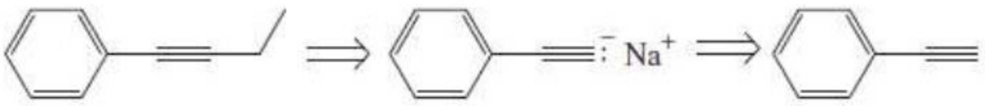
(a) *Retrosynthetic Analysis*



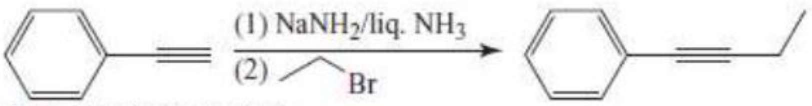
Synthesis



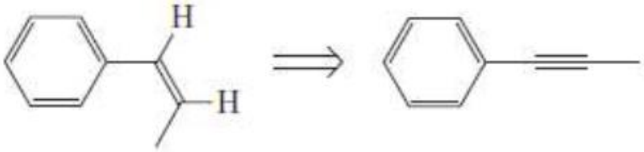
(b) *Retrosynthetic Analysis*



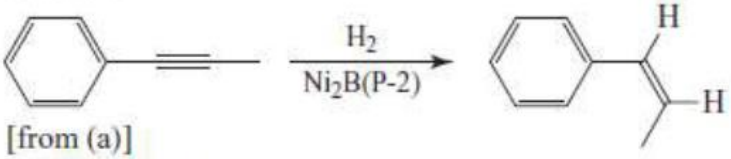
Synthesis



(c) *Retrosynthetic Analysis*

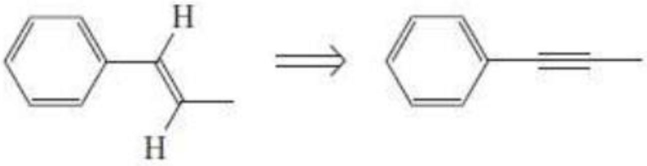


Synthesis

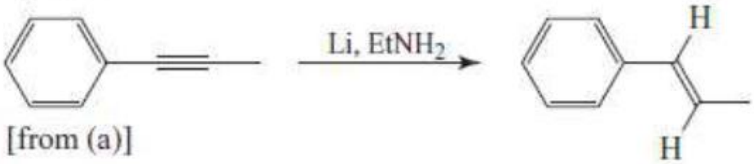


[from (a)]

(d) *Retrosynthetic Analysis*



Synthesis



[from (a)]

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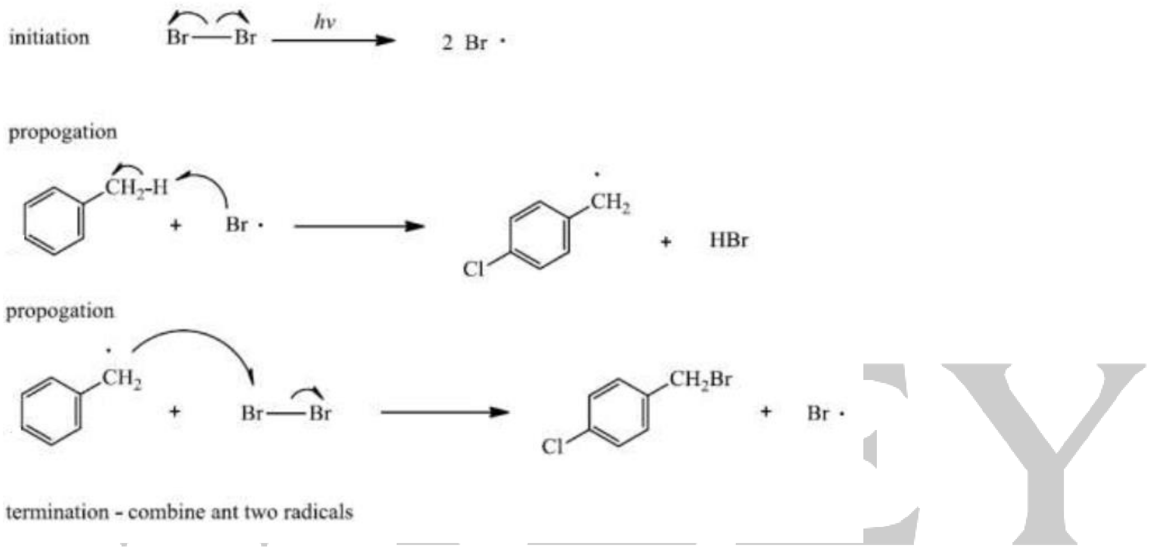
Review Problems

Radical Mechanisms and Properties

9.10



9.11

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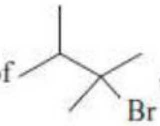
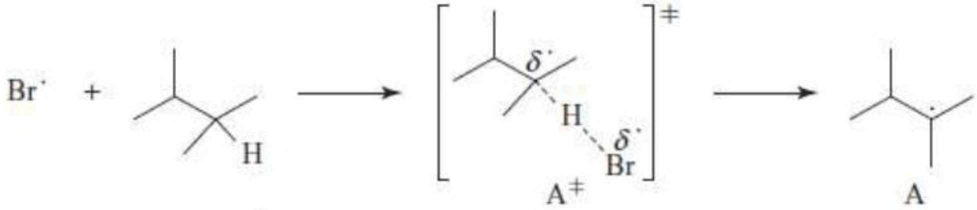
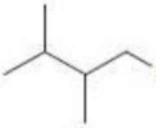
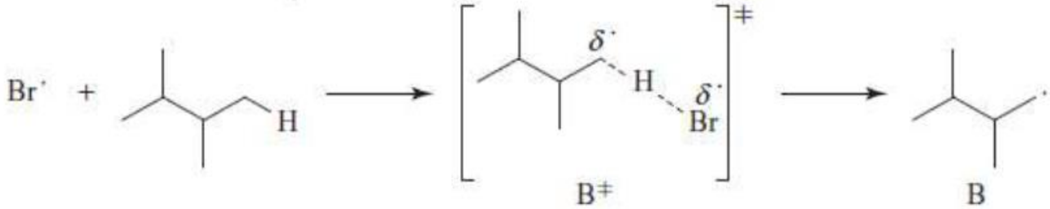
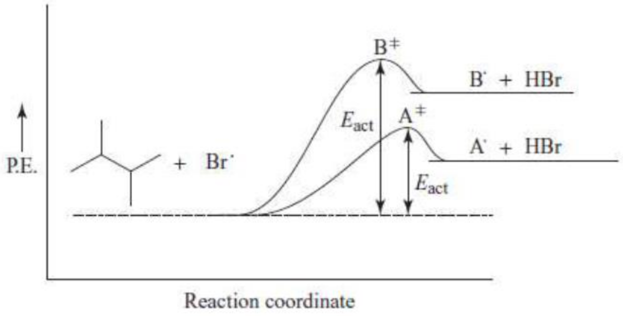
For formation of , the rate-determining step is:



For formation of  Br, the rate-determining step is:



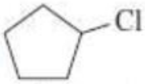


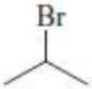
A• is a 3° alkyl radical and more stable than B•, a 1° alkyl radical, a difference anticipated by the relative energies of the transition states.

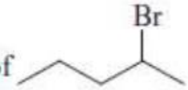
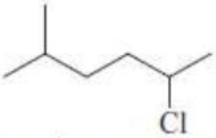
As indicated by the potential energy diagram, the activation energy for the formation of A‡ is less than that for the formation of B‡. The lower energy of A‡ means that a greater fraction of bromine atom-alkane collisions will lead to A• rather than to B•.

Note there is a statistical advantage to the formation of B• (6:1) but this is outweighed by the inherently greater reactivity of a 3° hydrogen.

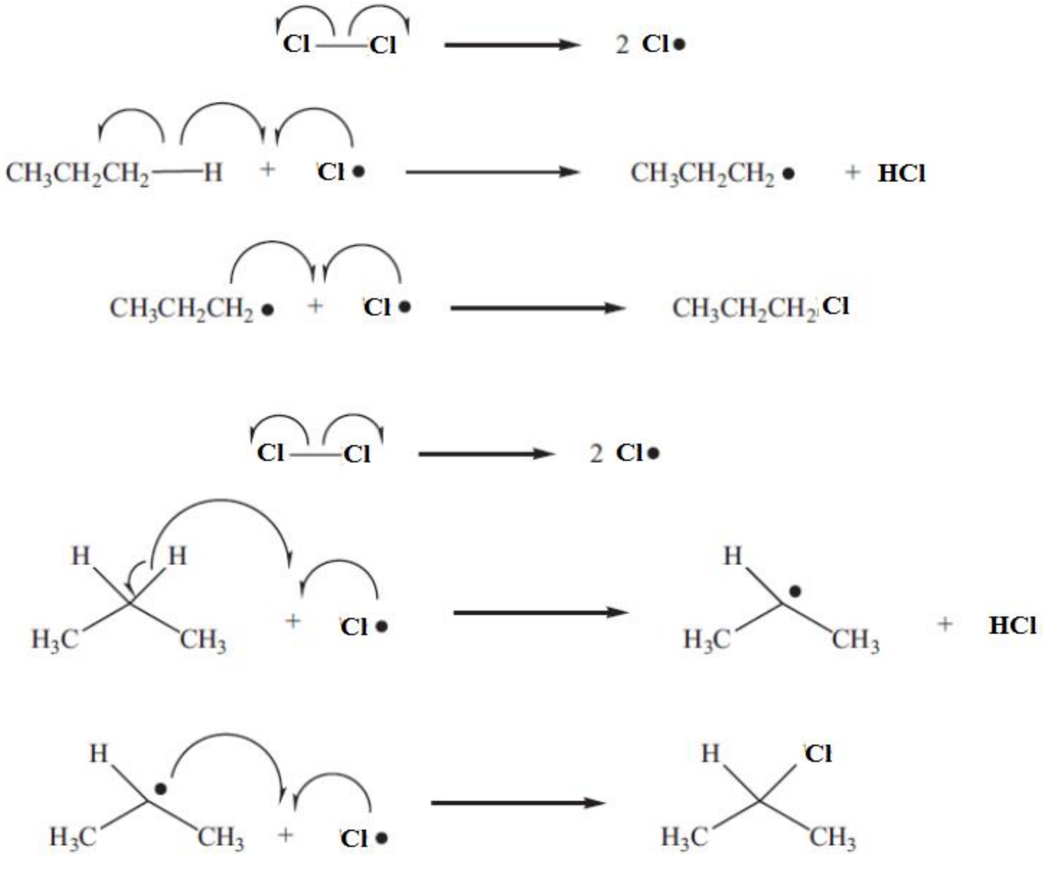
9.12

 and are the only monosubstitution products which can be formed from cyclopentane and ethane, respectively. (However, direct iodination of alkanes is not a feasible reaction, practically speaking.)

and  would be formed in amounts much larger than the isomeric alternatives due to the highly selective nature of bromine.

Formation of  and  would be acompanied by considerable amounts of isomeric byproducts in each case.

9.13



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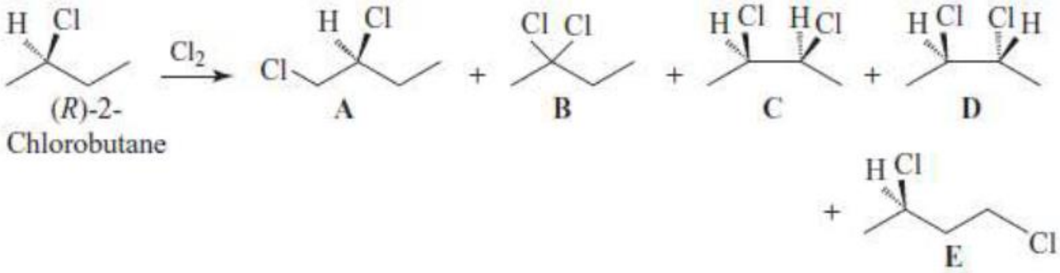
9.14

(a) Five



(b) Five. None of the fractions would be a racemic form.

(c) The fractions containing **A**, **D**, and **E**. The fractions containing **B** and **C** would be optically inactive. (**B** contains no chirality center and **C** is a meso compound.)

9.15

(a) Oxygen-oxygen bonds are especially weak, that is,

$$HO—OH \qquad DH° = 214 \text{ kJ mol}^{-1}$$
$$CH_3CH_2O—OCH_3 \qquad DH° = 184 \text{ kJ mol}^{-1}$$

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This means that a peroxide will dissociate into radicals at a relatively low temperature.

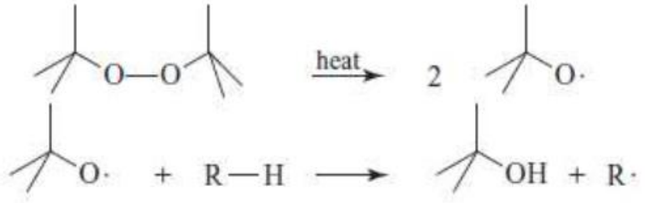
$$RO—OR \xrightarrow{100\text{-}200\,°C} 2\ RO\cdot$$

Oxygen-hydrogen single bonds, on the other hand, are very strong. (For HO—H, $DH° = 499$ kJ mol^{-1}.) This means that reactions like the following will be highly exothermic.

$$RO\cdot + R—H \longrightarrow RO—H + R\cdot$$

(b) *Step 1*

Step 2



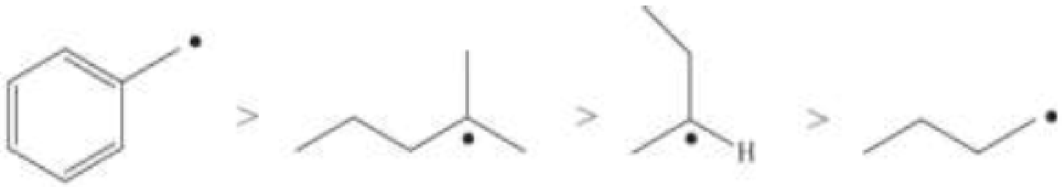
Chain Initiation

Step 3 $R\cdot + Br—Br \longrightarrow R—Br + Br\cdot$

Step 4 $Br\cdot + R—H \longrightarrow H—Br + R\cdot$

Chain Propagation

9.16



9.17

	$DH°$(kJ mol^{-1})
$CH_2=CH—H$	465
$(CH_3)_2CH—H$	413
$CH_2=CHCH_2—H$	369

(a) It is relatively difficult to effect radical halogenation at H_a because of the large $DH°$ for dissociation of a bond to an alkenyl (vinylic) hydrogen.

(b) Substitution of H_b occurs more readily than H_c because $DH°$ for the generation of an allylic radical is significantly smaller than that for the formation of a simple 2° radical.

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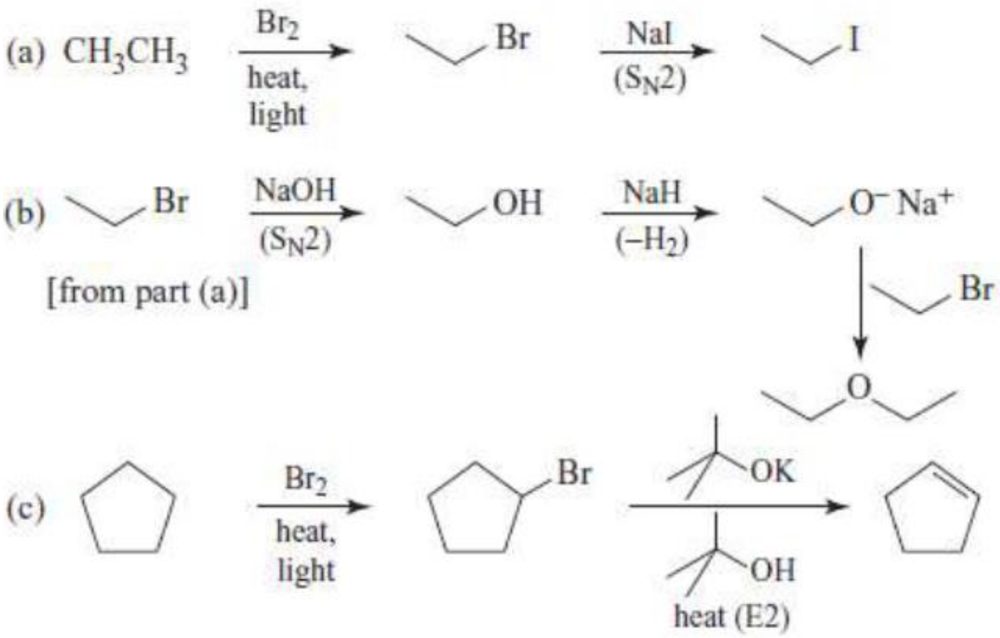
Synthesis

9.18



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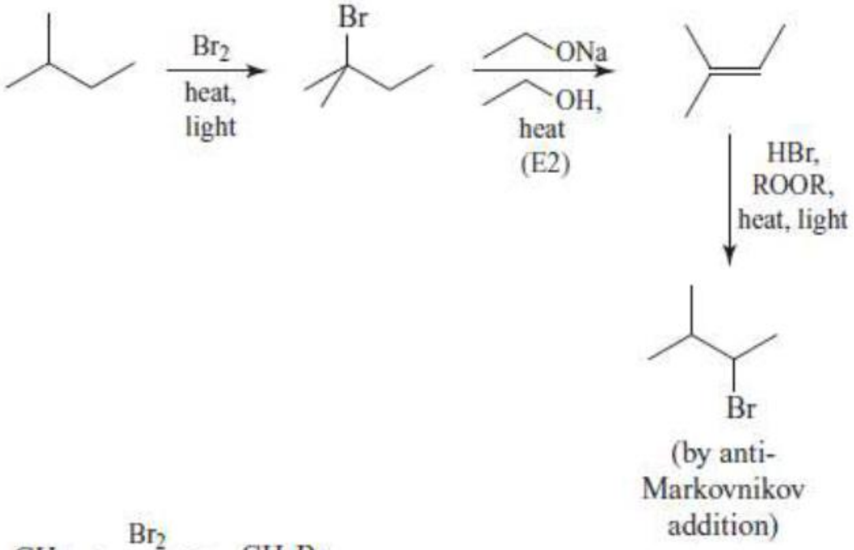
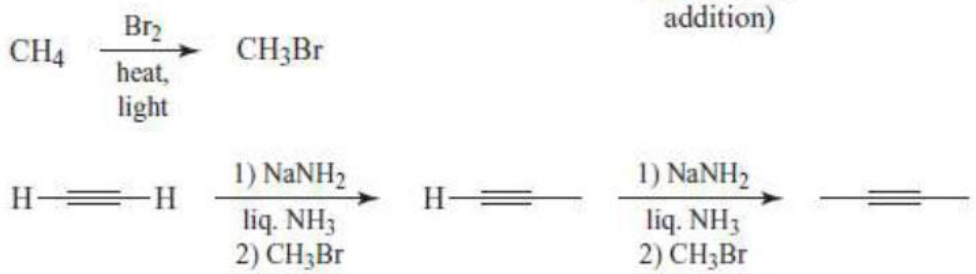
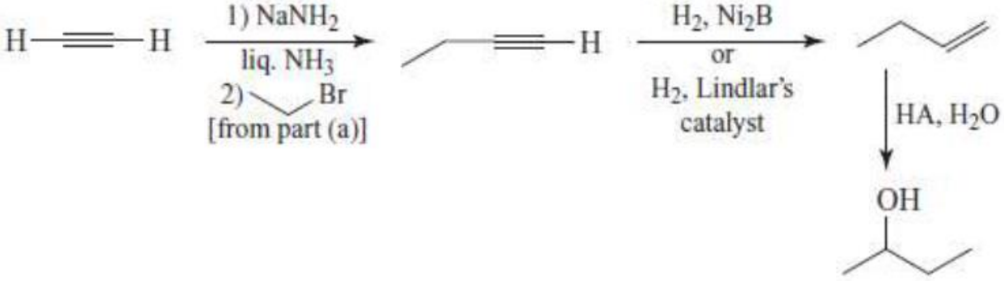
(d)



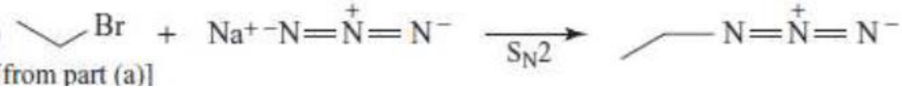
(e)



(f)



(g)



9.19

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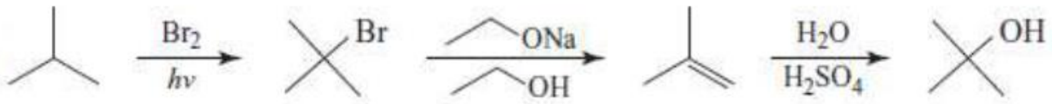
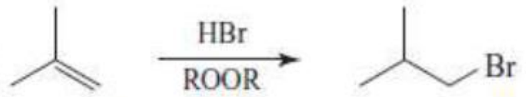
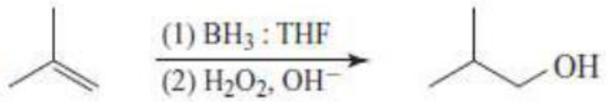
(a) 

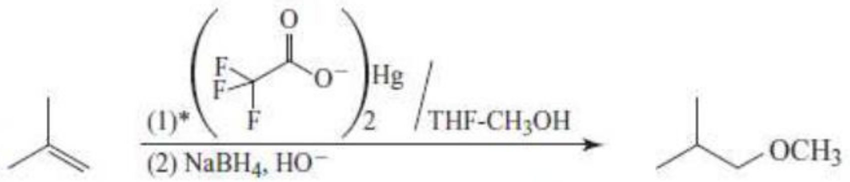
(aqueous solvolysis of 2-bromo-2-methylpropane would also yield the desired alcohol)

(b) 

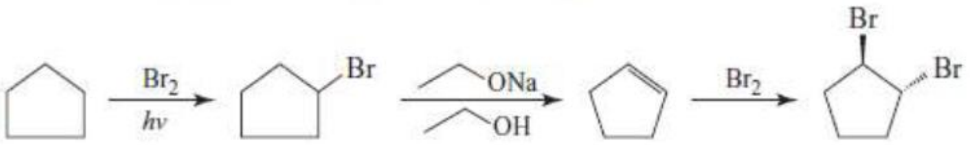
[from (a)]

(c) 

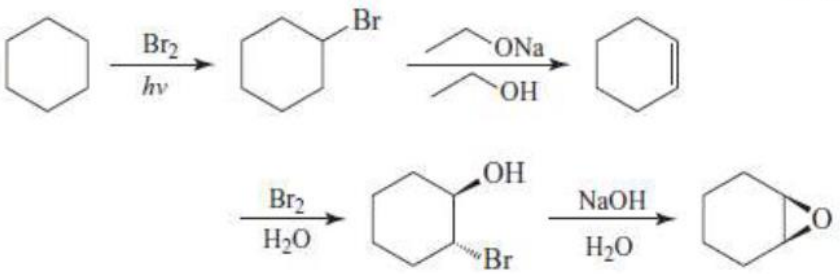
[from (a)]

(d) 

[from (a)] *[$Hg(OAc)_2$ would also work in step (1)]

(e) 

+ enantiomer

(f) 

+ enantiomer

9.20

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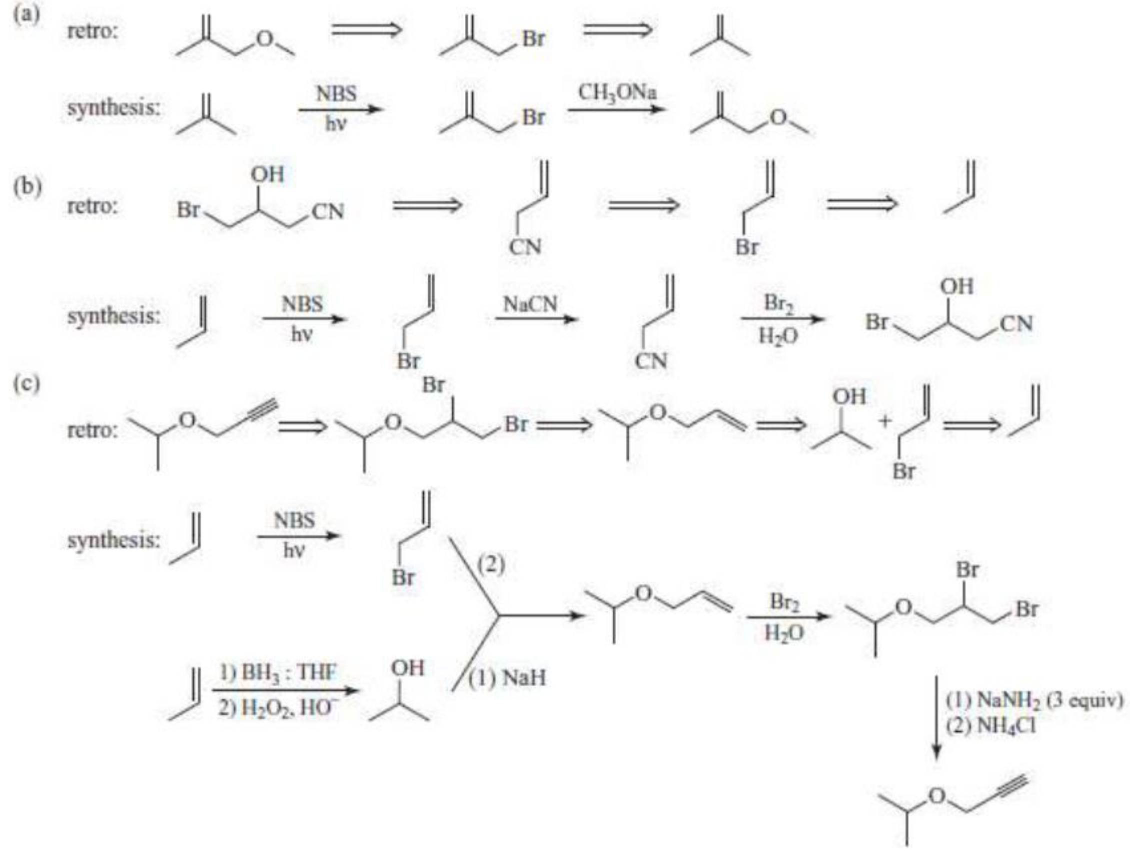

9.21

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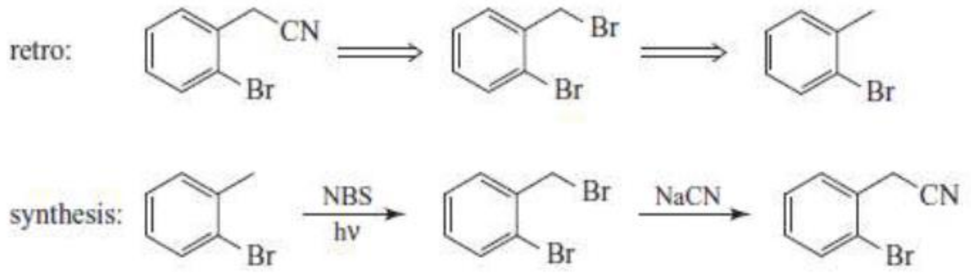
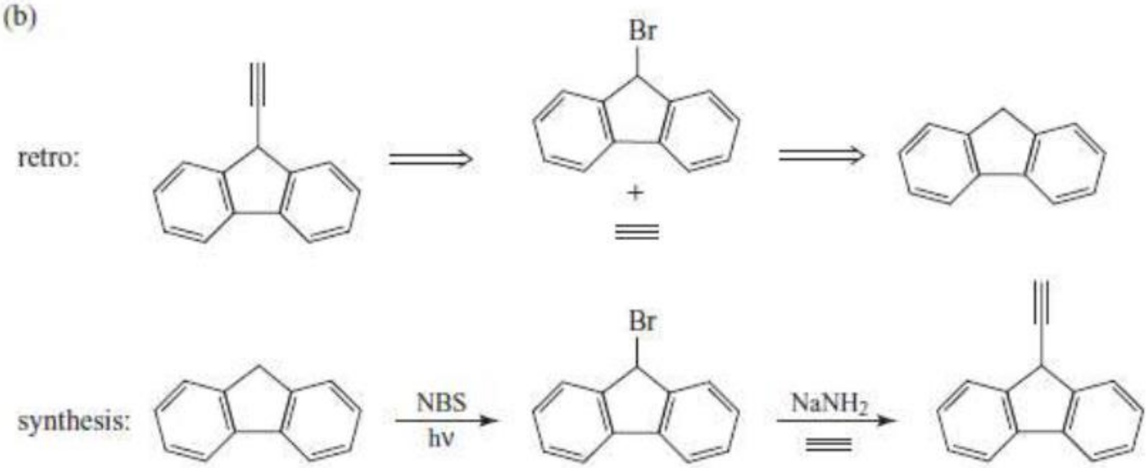
(a)



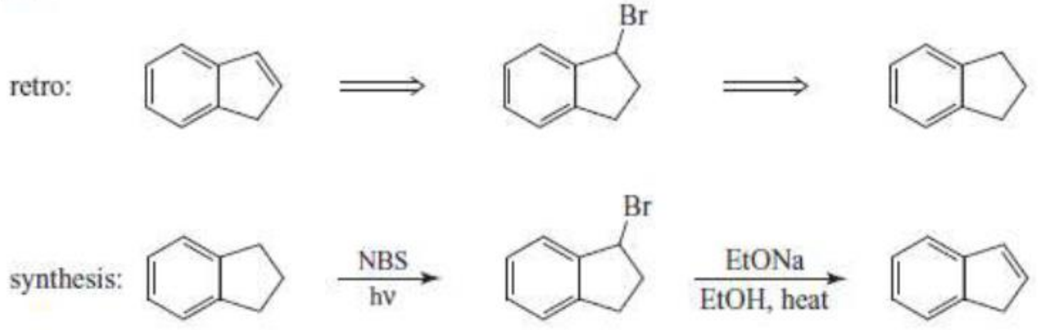
retro:
CN
Br
Br
Br
Br
synthesis:
Br
NBS
hν
Br
Br
NaCN
CN
Br

(b)



retro:
Br
+
synthesis:
NBS
hν
Br
NaNH$_2$

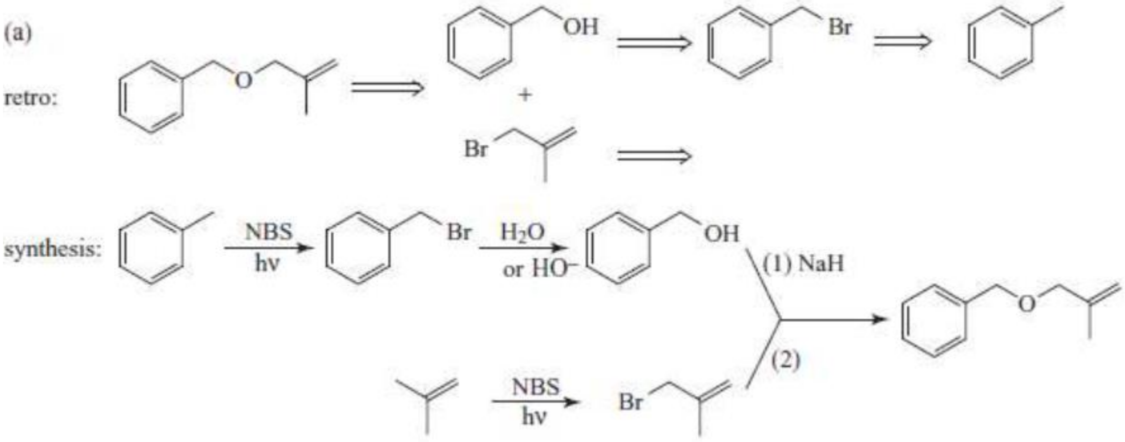
(c)



retro:
Br
synthesis:
NBS
hν
Br
EtONa
EtOH, heat

9.22

(a)



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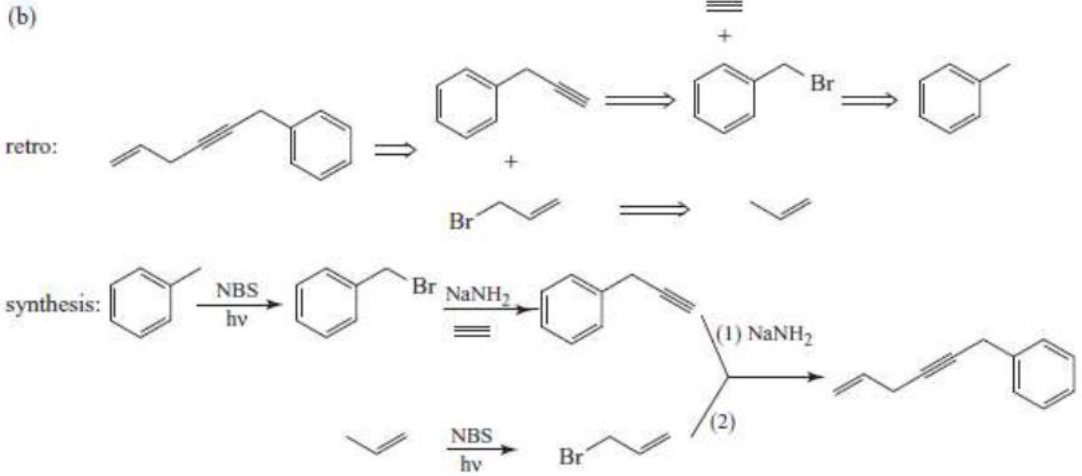

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. **(d)** It is free radical addition at the position of most stable free radical.
2. **(b)** The other three products would be possible by reaction between the ethyl free radical and the propyl free radical intermediate.
3. **(c)** Only HBr gives anti-Markovnikov addition as all its steps are exothermic.
4. **(b)** It is anti-Markovnikov addition.
5. **(a)** Only one of the H will be replaced with Cl in excess of Methane.
6. **(b)** Most stable free radical would be formed.
7. **(d)** It is intramolecular Wurtz reaction.
8. **(c)** Only HBr gives anti-Markovnikov addition.
9. **(d)** It is intramolecular Wurtz reaction.

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10. **(b)** Enantiomers cannot be separated by fractional distillation.
11. (d) Substitution would take place at the position where the most stable free radical is formed.
12. **(b)** It is anti-Markovnikov addition.
13. **(a)** The product 1-chloro-2-methylbutane would exist in two enantiomeric forms.

14. **(a)** Br would replace the indicated H atom, and the products formed would be enantiomers due to sp^2 hybridized free radical intermediate.
15. **(d)** Substitution would take place at the position where the most stable free radical is formed.
16. **(b)** Substitution would take place at the position where the most stable free radical is formed.
17. **(b)** This alternative step has a more endothermic ΔH^o than the first.

18. (b) It is intramolecular Wurtz reaction.
19. **(d)** Neo-pentane ($(CH_3)_3C$) has only one type of H atom that can be substituted.
20. **(b)** It is intramolecular Kolbe Electrolysis.

21. **(b)** 2-chlorobutane formed would exist in two enantiomeric forms.
22. **(d)** The C-H bond is partially broken in transition state.

<H2> Linked Comprehension Type

1. **(a)** The correct transition state is a.

2. **(c)** Five products: 1,2-dichloro butane (optically active); 2,2-dichloro butane (meso); 2,3-dichloro butane (one meso and one optically active); 1,3-dichloro butane (optically active).

3. **(b)** R is 2 (enantiomers of 2-chloropentane); S is 3 (1,2-dichloro butane (op. active); 2,2-dichloro butane (meso); 2,3-dichloro butane (one meso and one optically active); 1,3-dichloro butane (optically active)); P is 2 (trans-1,2-dichlorocyclobutane); Q is 2 (1-chloro-2-methoxypropane).

<H2> Integer Type

1. **(4)** Two enantiomers of 1-chloro-2-methylbutane and two enantiomers of 2-chloro-3-methylbutane.

2. **(4)** Products are: 1-chloropentane; 2-chloropentane (two enantiomers); and 3-chloropentane.

3. **(5)** Substitute Cl atom at 1,2,3 (2 diastereomers) and 4 positions.

4. **(7)** Products: 1,1-dichlorocyclopentane; cis-1,2-dichlorocyclopentane and trans-1,1-dichlorocyclopentane (2 enantiomers); cis-1,3-dichlorocyclopentane and trans-1,3-dichlorocyclopentane (2 enantiomers).

5. **(6)** Products: 1-chloro-4-propylheptane; 2-chloro-4-propylheptane (enantiomers at the C-2 position); 3-chloro-4-propylheptane (enantiomers at the C-3 position); and

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4-chloro-4-propylheptane.

6. **(3)** Products: 1-chloro-2,3-dimehtylbutane (2 enantiomers) and 2-chloro-2,3-dimethylbutane.

<H2> Matrix Match Type

1. $a \rightarrow (q, x); b \rightarrow (s, z); c \rightarrow (p, w); d \rightarrow (q, x)$

Option (a): Cl at bridgehead position and adjacent to bridgehead position (2 enantiomers).

Option (b): 1-chloro-2-methyl butane and 2-chloro-3-methylbutane would exist as enantiomers.

Option (c): Only product is 1-chloro-2,2,3,3-tetramethylbutane.

Option (d): 2-chlorobutane will exist as two enantiomers.

2. $a \rightarrow (p, r, s); b \rightarrow (q, r, s); c \rightarrow (q, r, s); d \rightarrow (p, r, s)$

All are intramolecular Wurtz reactions with free radicals as intermediate.

3. $a \rightarrow (s); b \rightarrow (r); c \rightarrow (p); d \rightarrow (q)$

All are Wurtz reaction with free radical as intermediate.

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Chapter 10: Alcohols and Ethers: Synthesis and Reactions

Practice Problems

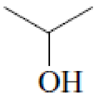
10.1

These names mix two systems of nomenclature (functional class and substitutive; see Section 4.3F). The proper names are: isopropyl alcohol (functional class) or 2-propanol (substitutive), and *tert*-butyl alcohol (functional class) or 2-methyl-2-propanol (substitutive). Names with mixed systems of nomenclature should not be used.

10.2

(a)

1-Propanol
or propan-1-ol
(Propyl alcohol)

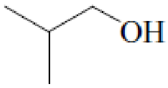


2-Propanol
or propan-2-ol
(Isopropyl alcohol)

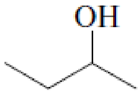
Methoxyethane
(Ethyl methyl ether)

(b)

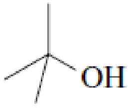
1-Butanol
or
butan-1-ol
(Butyl alcohol)



2-Methyl-1-propanol
or
2-methylpropan-1-ol
(Isobutyl alcohol)



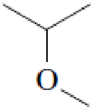
2-Butanol
or
butan-2-ol
(*sec*-Butyl alcohol)



2-Methyl-2-propanol
or
2-methylpropan-2-ol
(*tert*-Butyl alcohol)

1-Methoxypropane
(Methyl propyl ether)

Ethoxyethane
(Diethyl ether)



2-Methoxypropane
(Isopropyl methyl ether)

10.3

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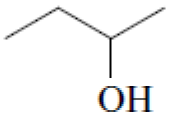
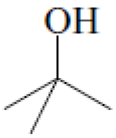
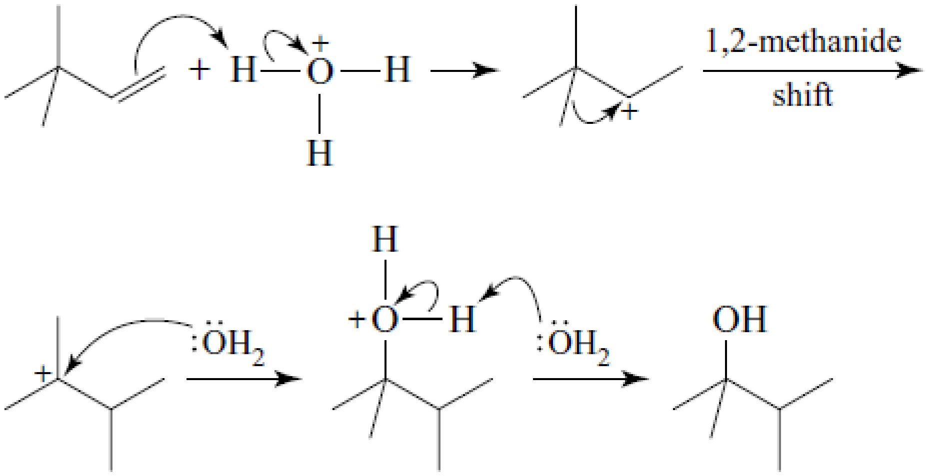
(a) 

(b)

(c) 

10.4

A rearrangement takes place.

(a) 

2,3-Dimethyl-2-butanol
(major product)

(b) (1) $Hg(OAc)_2$/THF-H_2O; (2) $NaBH_4$, HO^-
(oxymercuration-demercuration)

10.5

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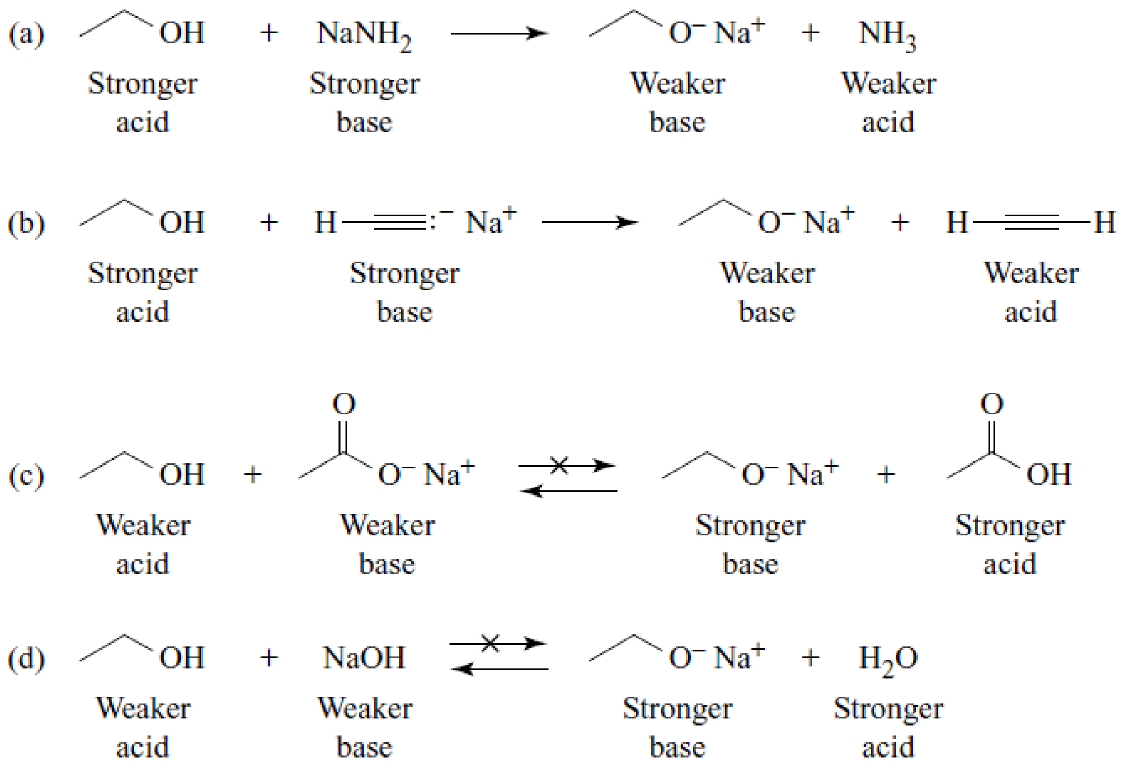

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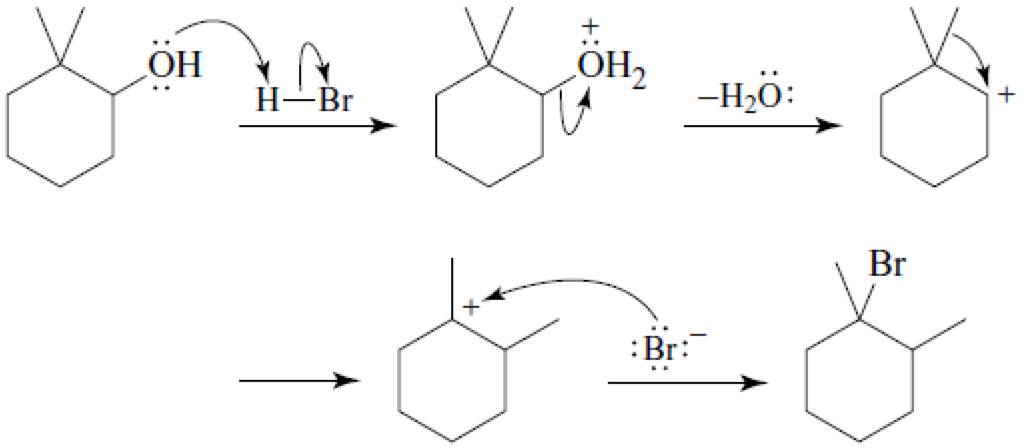
10.6



10.7

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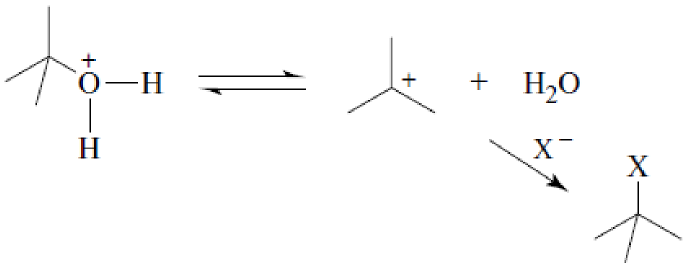
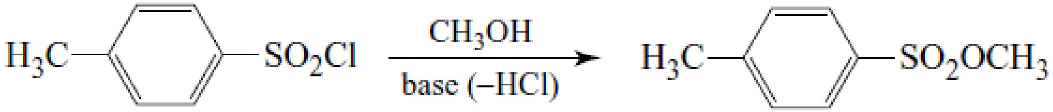
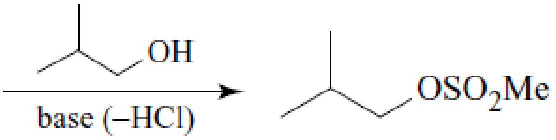
(a) Tertiary alcohols react faster than secondary alcohols because they form more stable carbocations; that is, 3° rather than 2°:

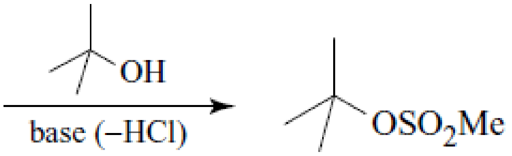


(b) CH_3OH reacts faster than 1° alcohols because it offers less hindrance to S_N2 attack. (Recall that CH_3OH and 1° alcohols must react through an S_N2 mechanism.)

10.8

(a) 

(b) CH_3SO_2Cl 

(c) CH_3SO_2Cl 

10.9

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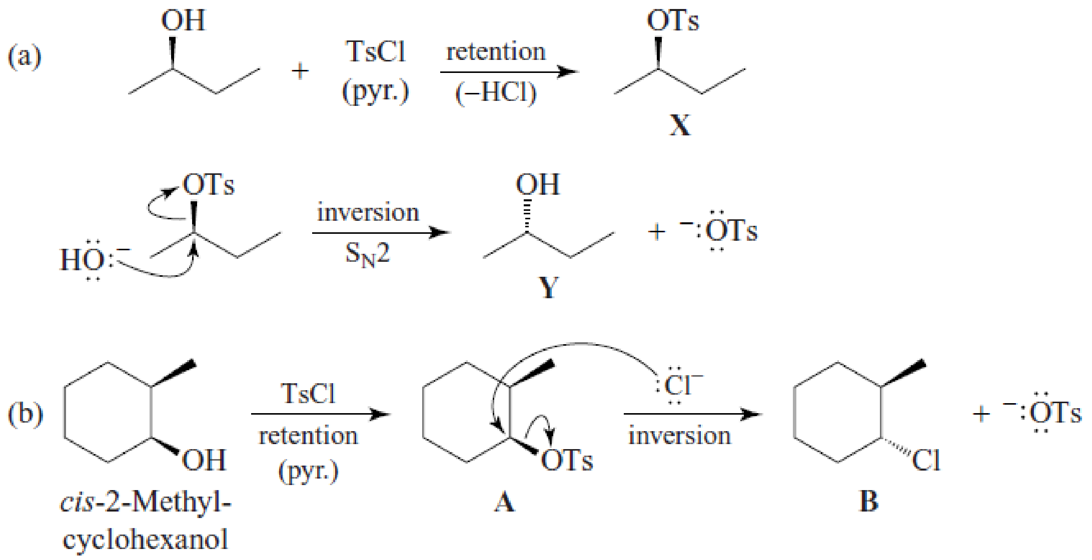
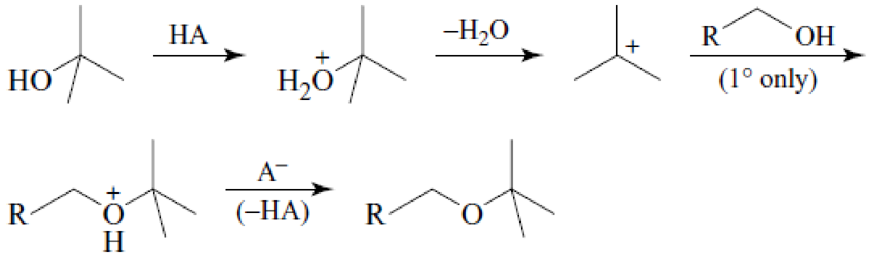


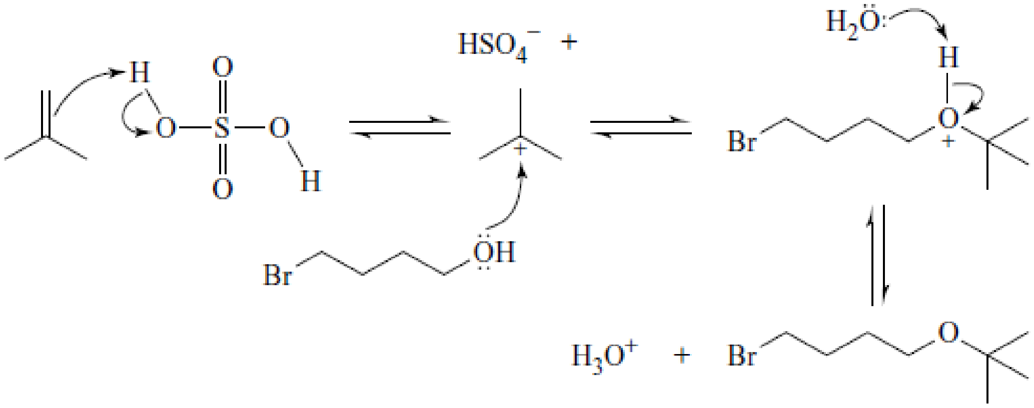
10.10



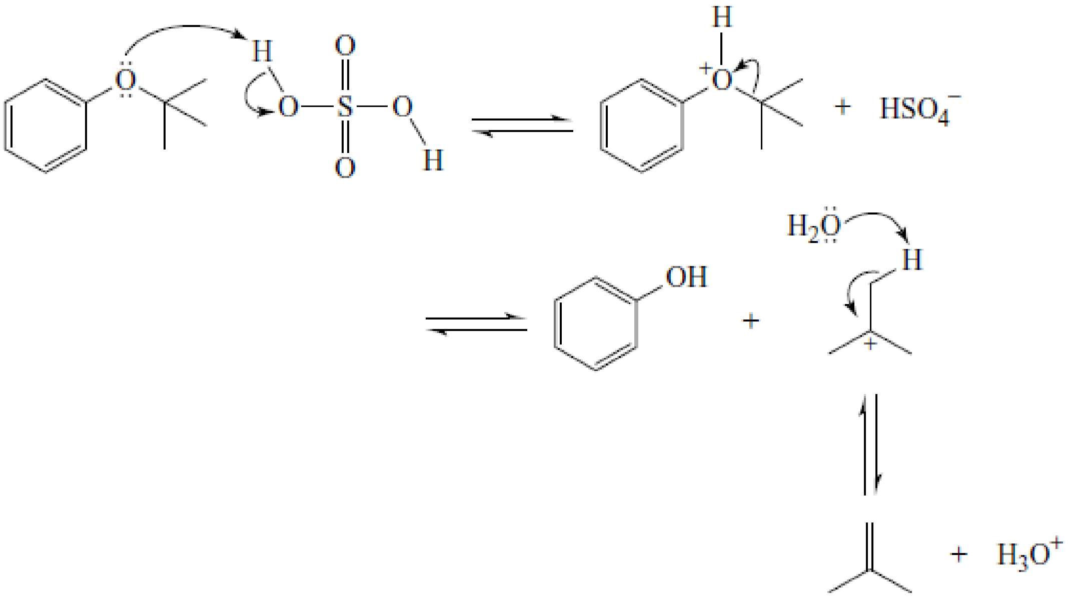
This reaction succeeds because a 3° carbocation is much more stable than a 1° carbocation. Consequently, mixing the 1° alcohol and H_2SO_4 does not lead to formation of appreciable amounts of a 1° carbocation. However, when the 3° alcohol is added, it is rapidly converted to a 3° carbocation, which then reacts with the 1° alcohol that is present in the mixture.

10.11

(a)

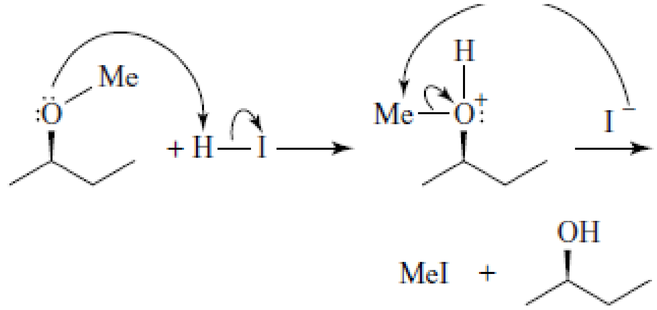

H
O
S
O
O
H
HSO4−
+
+
Br
ÖH
H2Ö:
H
O
+
Br
H3O+
+
Br
O

(b)


Ö
H
O
S
O
O
O
H
H
+O
+
HSO4−
OH
+
H2Ö
H
+
+
H3O+

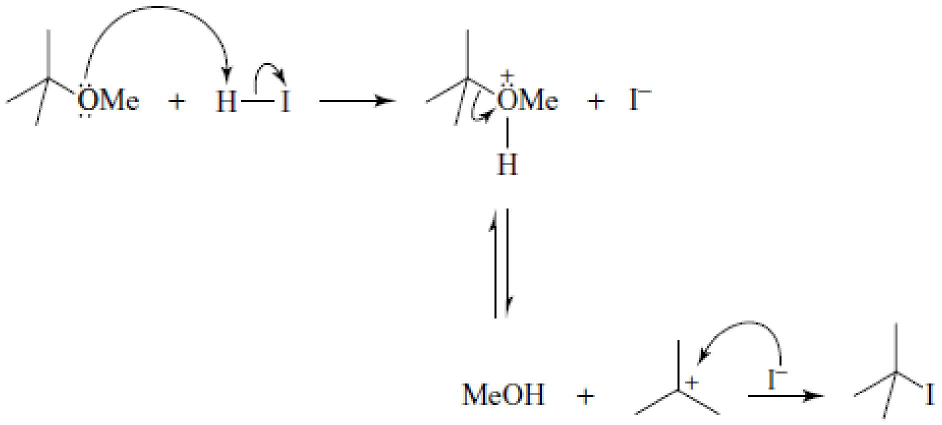
10.12

(a)



S_N2 attack by I^- occurs at the methyl carbon atom because it is less hindered; therefore, the bond between the *sec*-butyl group and the oxygen is not broken.

(b)



In this reaction the much more stable *tert*-butyl cation is produced. It then combines with I^- to form *tert*-butyl iodide.

10.13

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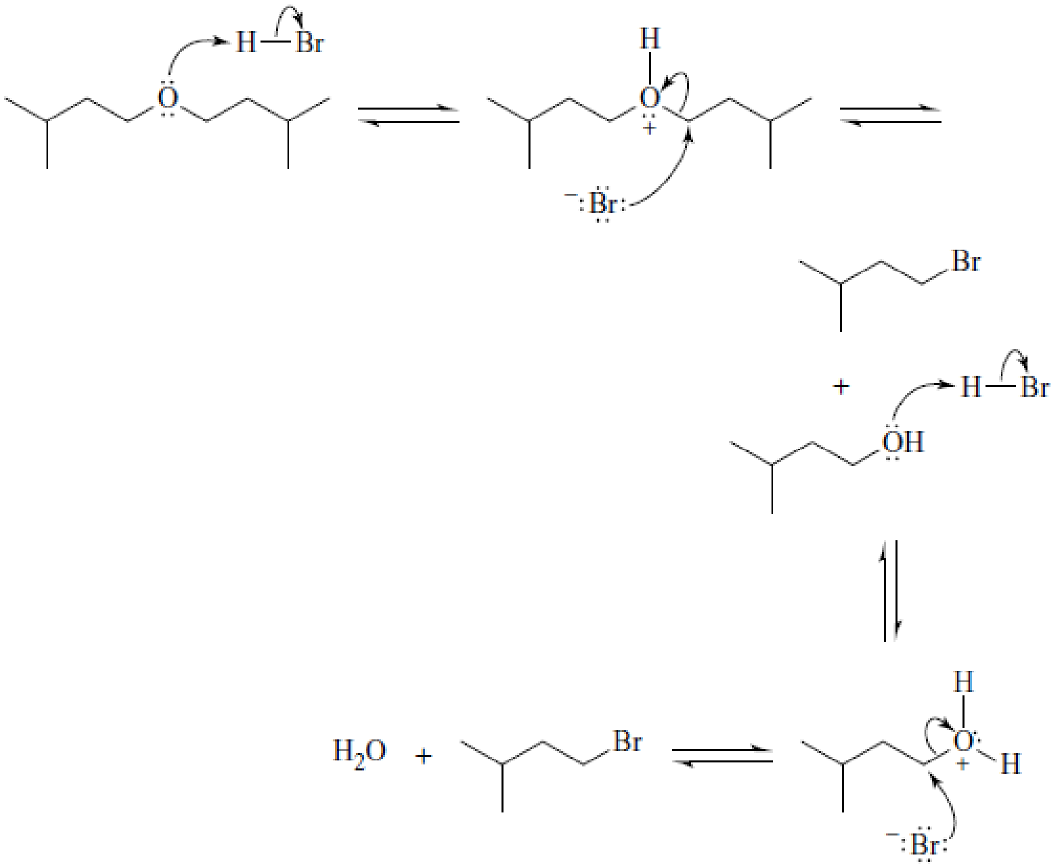

10.14

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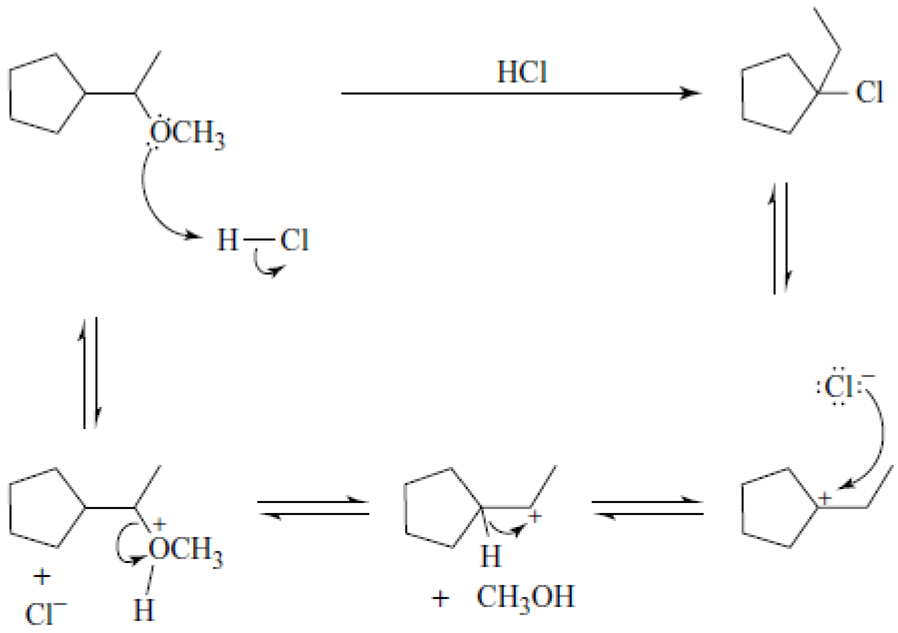

10.15

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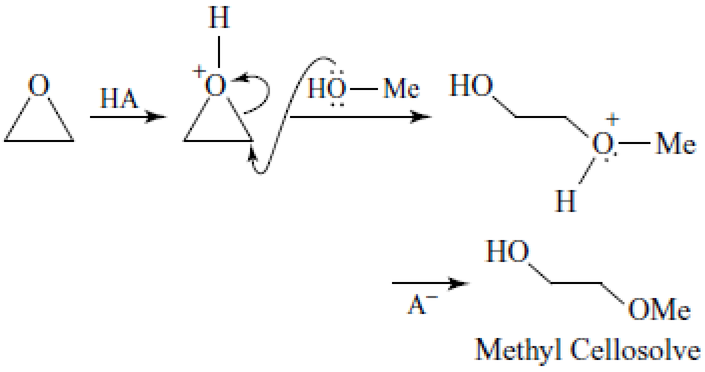
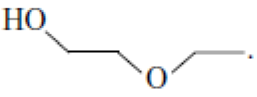
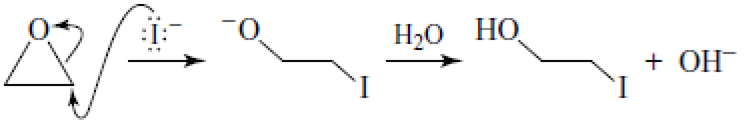
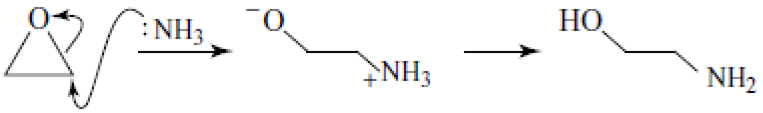
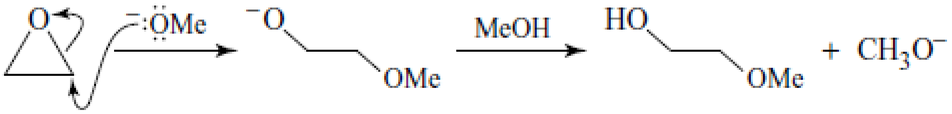
(a) 

(b) An analogous reaction yields ethyl cellosolve, 

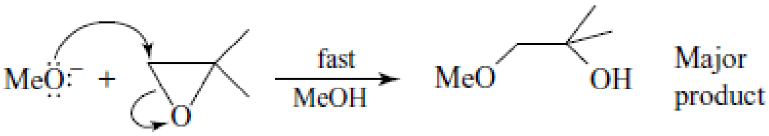
(c) 

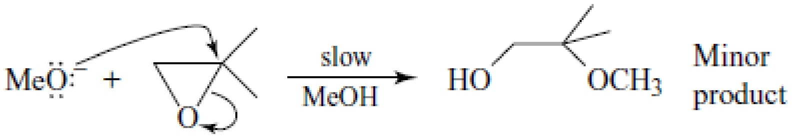
(d) 

(e) 

10.16

The reaction is an S_N2 reaction, and thus nucleophilic attack takes place much more rapidly at the primary carbon atom than at the more hindered tertiary carbon atom.





10.17

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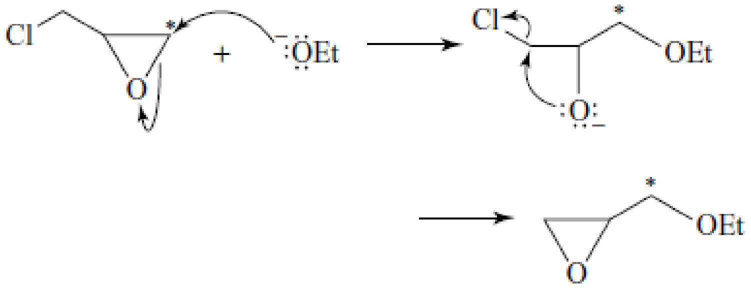
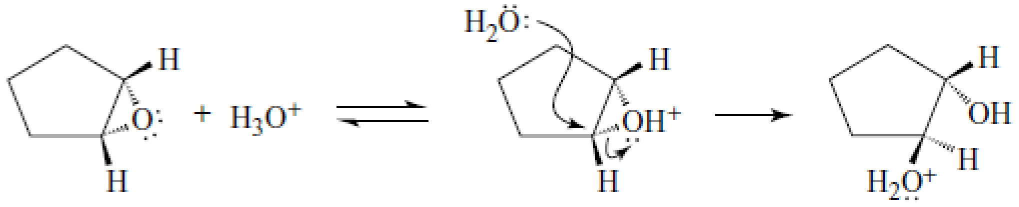
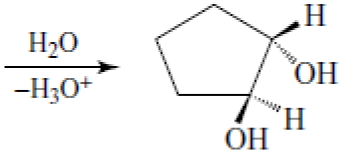
Ethoxide ion attacks the epoxide ring at the primary carbon because it is less hindered, and the following reactions take place.



10.18

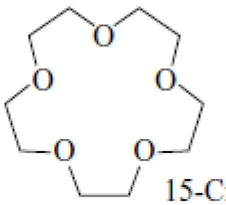




(plus enantiomer, by attack at the other epoxide carbon)

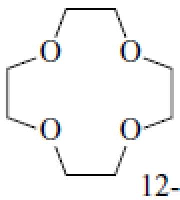
10.19

(a)



15-Crown-5

(b)



12-Crown-4

Review Problems

Nomenclature

10.20

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(a) 3,3-Dimethyl-1-butanol or 3,3-dimethylbutan-1-ol

(b) 4-Penten-2-ol or pent-4-en-2-ol

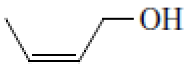
(c) 2-Methyl-1,4-butanediol or 2-methylbutan-1,4-diol

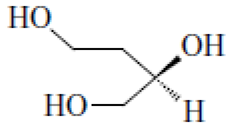
(d) 2-Phenylethanol

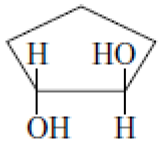
(e) 1-Methylcyclopentanol

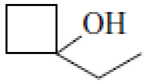
(f) *cis*-3-Methylcyclohexanol

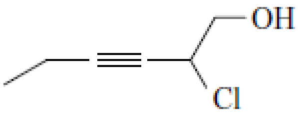
10.21

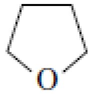
(a) 

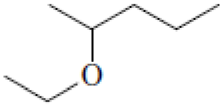
(b) 

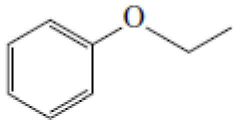
(c) 

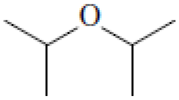
(d) 

(e) 

(f) 

(g) 

(h) 

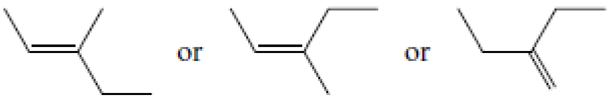
(i) 

(j)

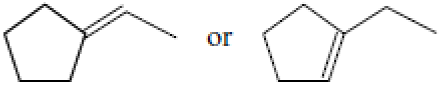
Reactions and Synthesis

10.22

(a)

(c) 

(b)

(d) 

10.23

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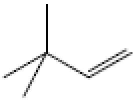
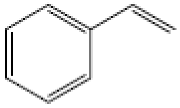
(a) 

(c) 

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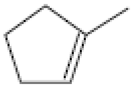
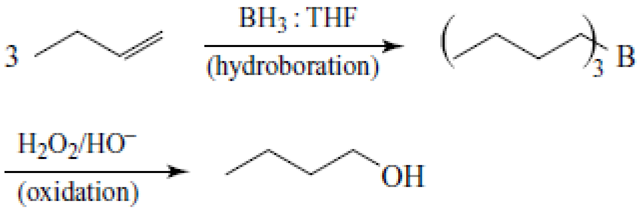
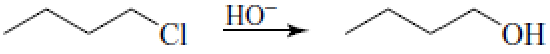
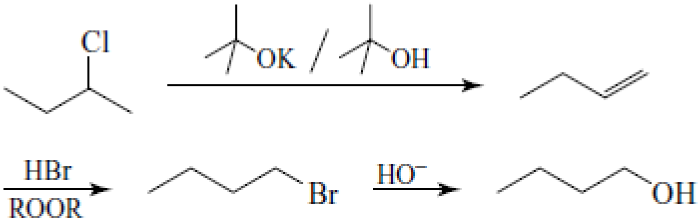
(d) 

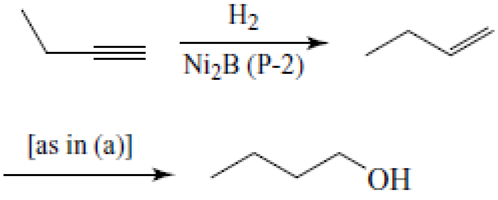
10.24

(a) 

(b) 

(c) 

(or by hydroboration-oxidation of 1-butene formed by the elimination reaction)

(d) 

10.25

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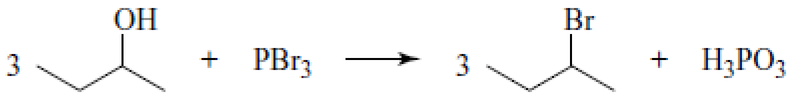
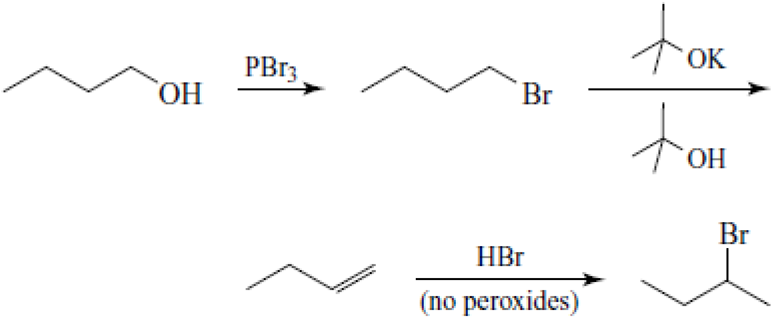
(a) 

(b) 

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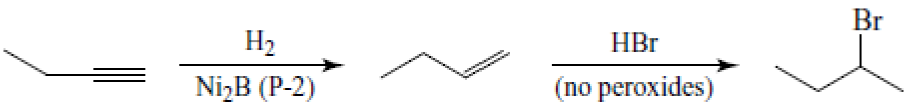
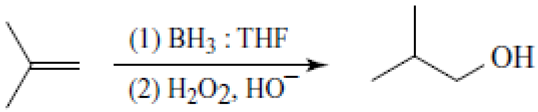
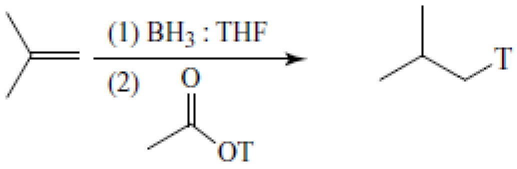
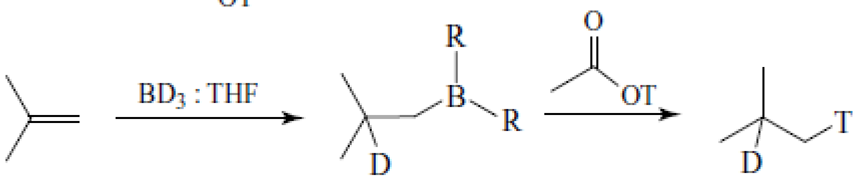
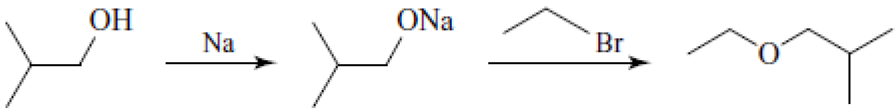
(d) 

10.26

(a) 

(b) 

(c) 

(d) 

[from (a)]

10.27

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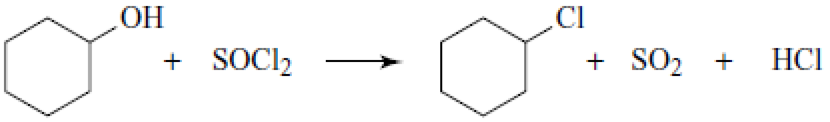
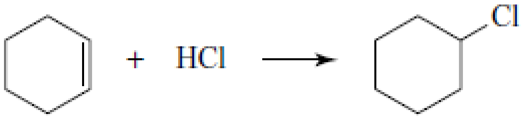
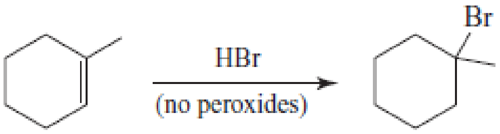
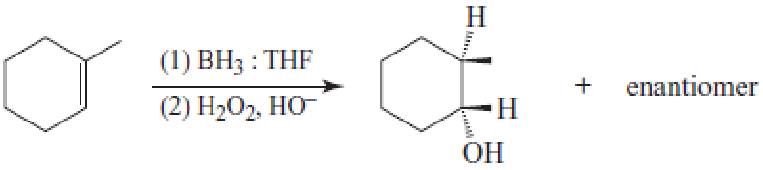
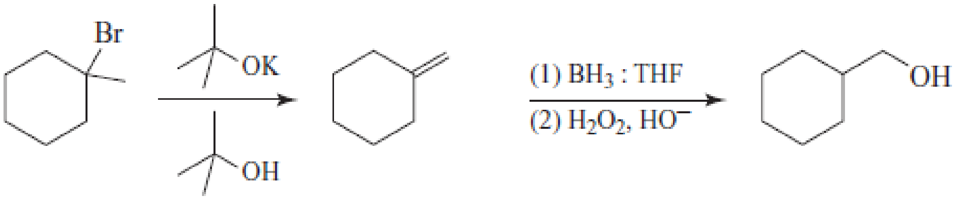
(a) 

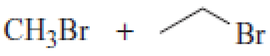
(b) 

(c) 

(d) 

(e) 

10.28

(a) 

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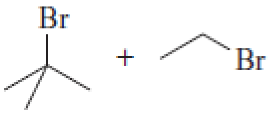
(b) 

(d) (2 molar equivalents)

10.29

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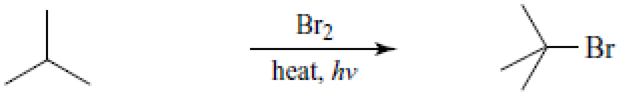
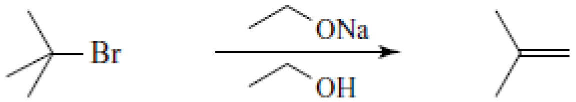
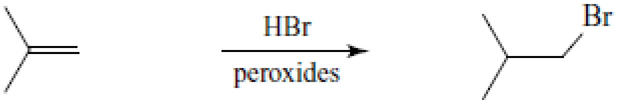
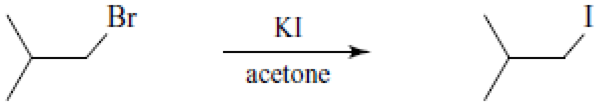
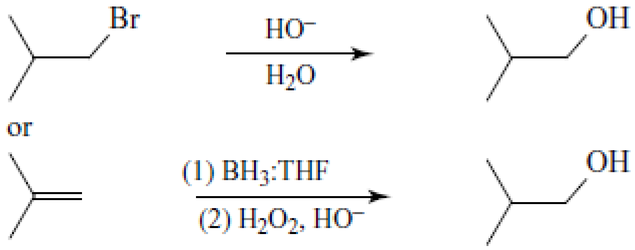
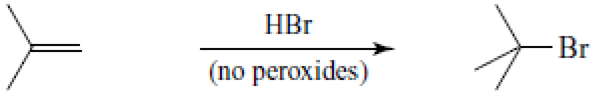
(a) 

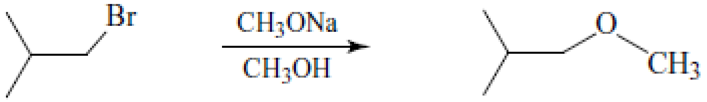
(b) 

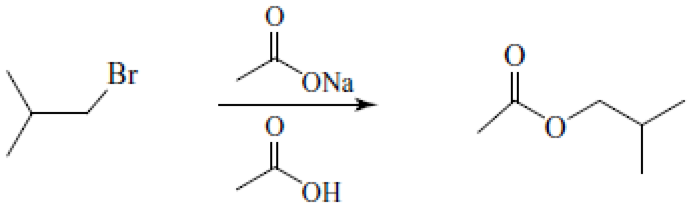
(c) 

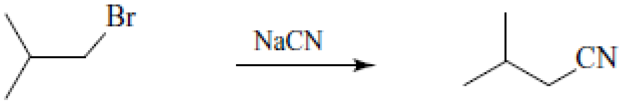
(d) 

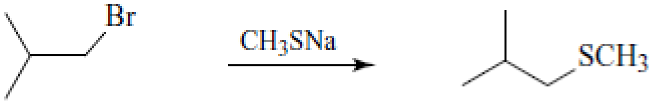
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

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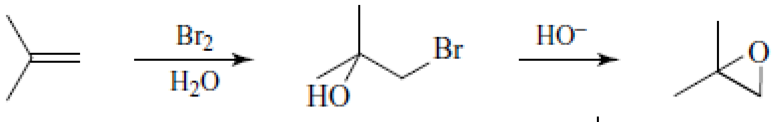
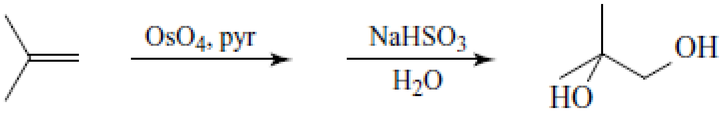
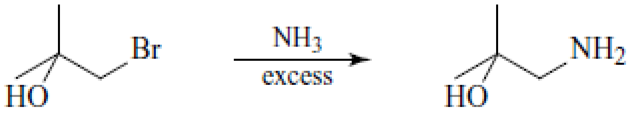
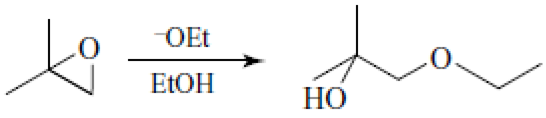
(k) 

(l) 

(m) 

(n) 

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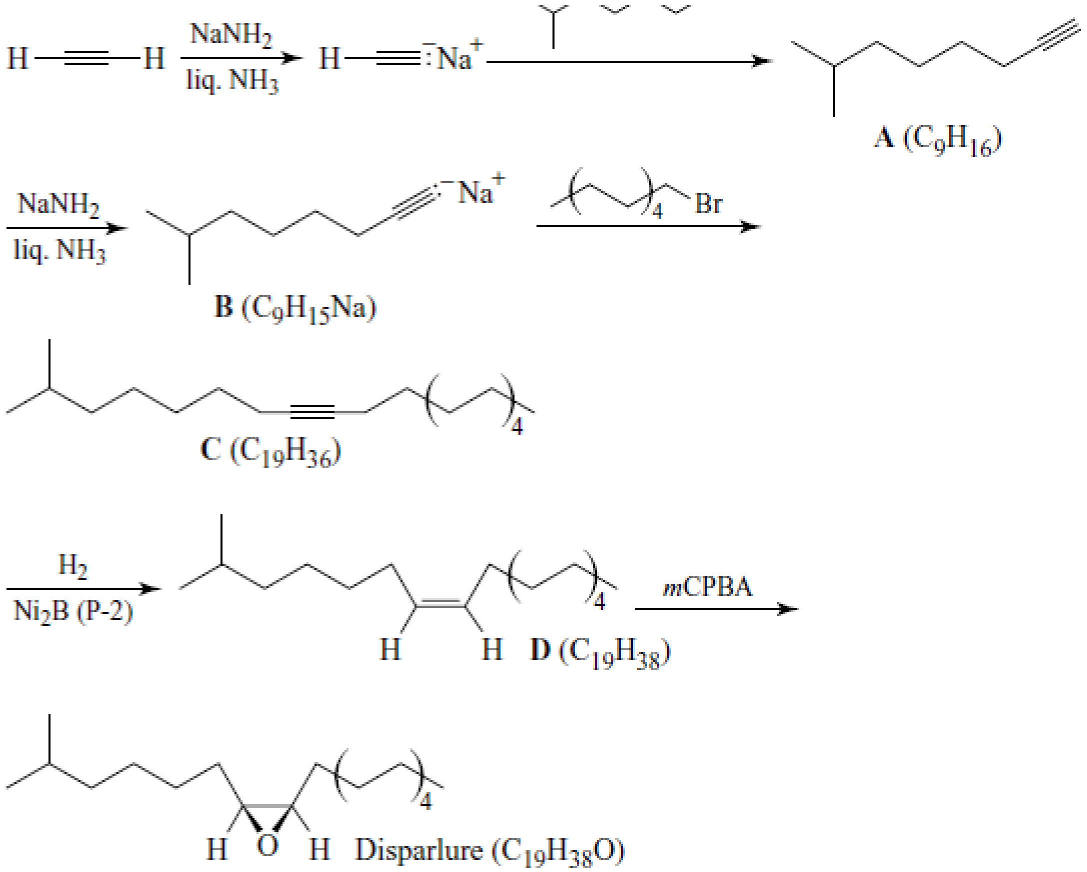

10.31

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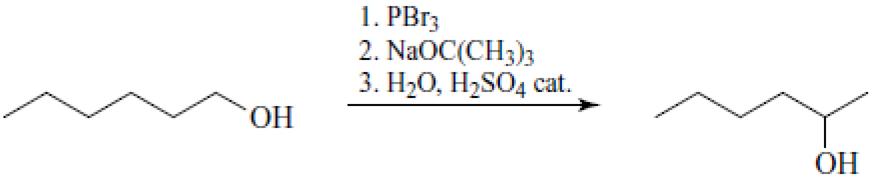
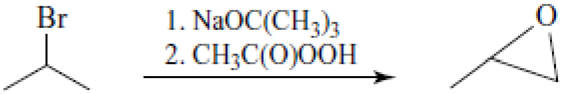
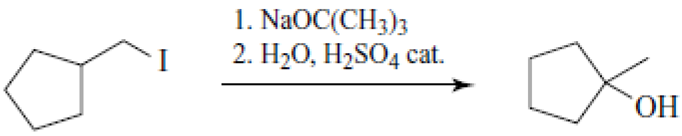
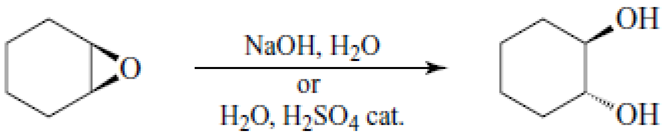
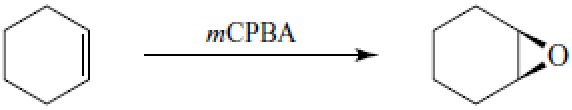
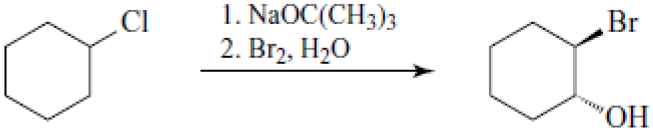
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

10.32

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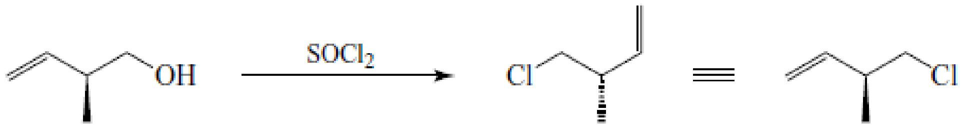
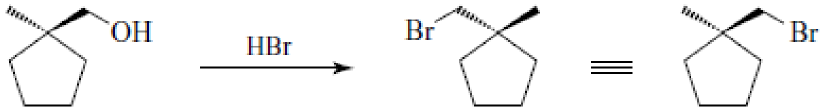
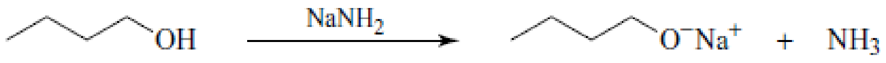
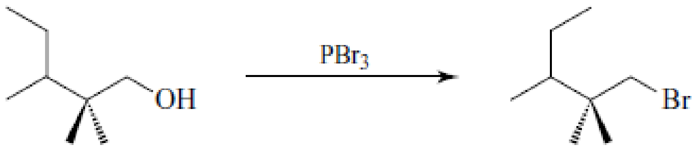
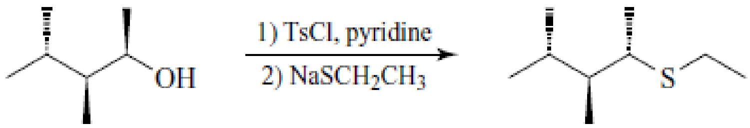
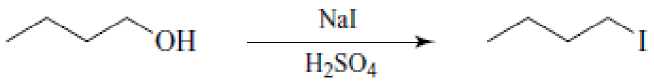
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

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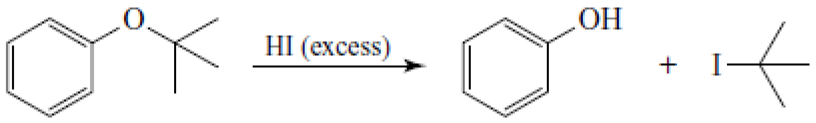
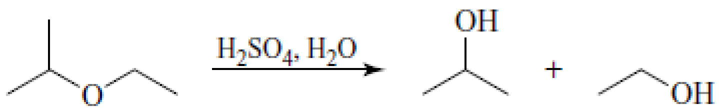
(a)

(b) 

(c) 

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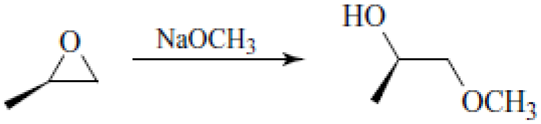
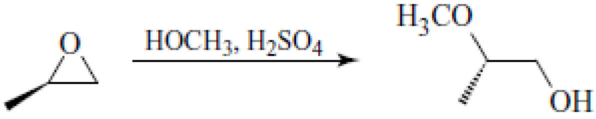
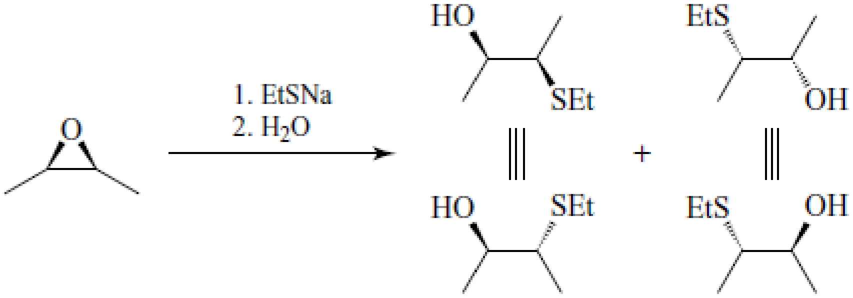
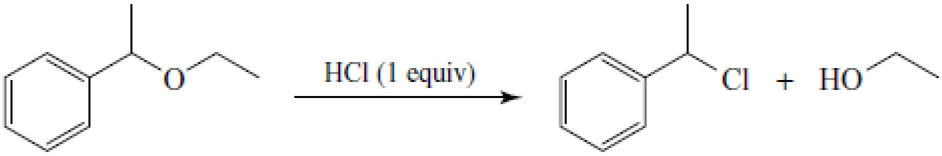
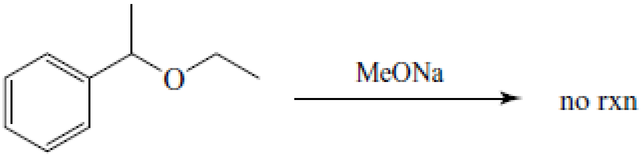
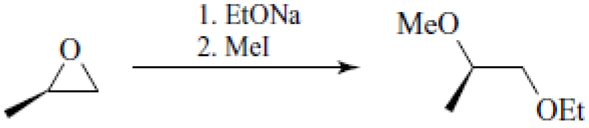
(d) 

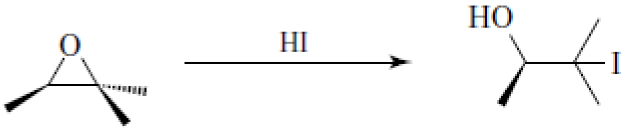
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

10.34

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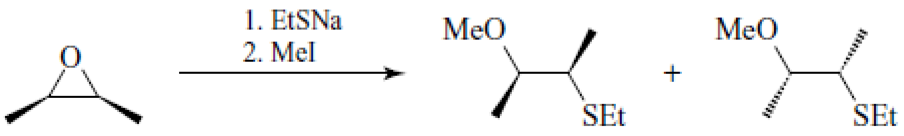
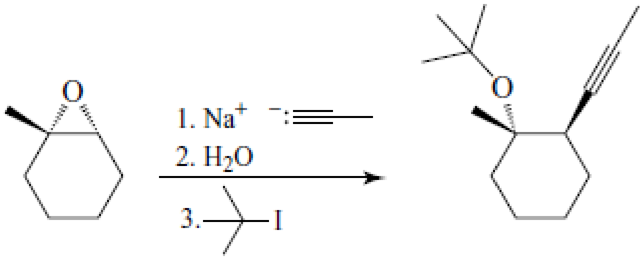
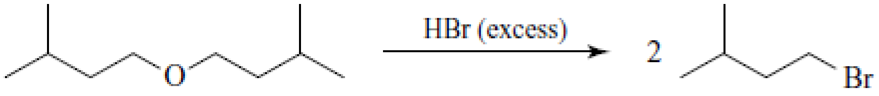
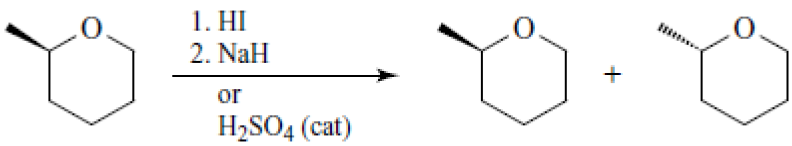
(a) 

(b) 

(c) 

(d) 

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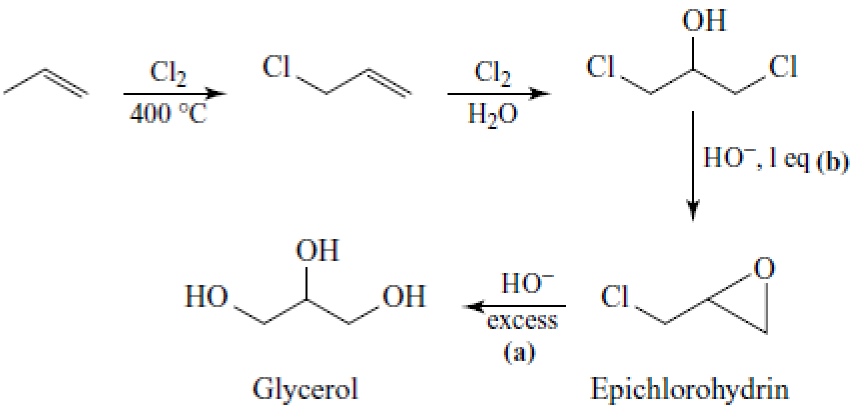
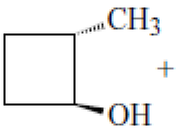
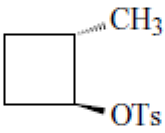
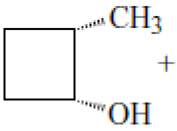
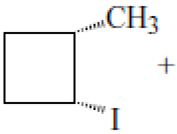
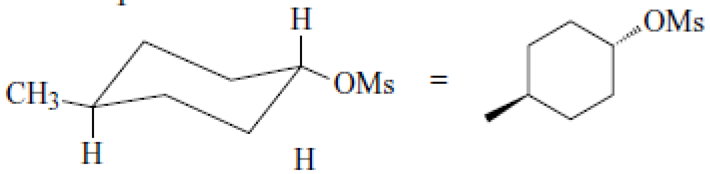


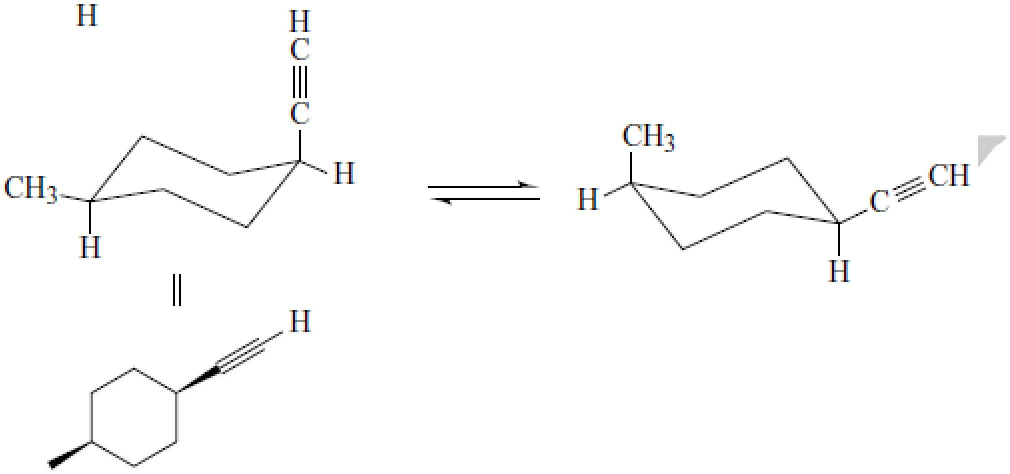
10.36

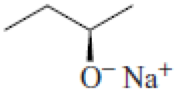
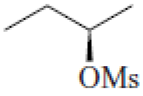
(a) **A** =  + enantiomer **B** =  + enantiomer

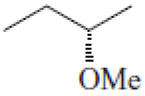
C =  + enantiomer

D =  + enantiomer **A** and **C** are diastereomers.

(b) **E** = 

F = 

(c) **G** =  **H** = **I** = 

J = 

H and **J** are enantiomers.

Mechanisms

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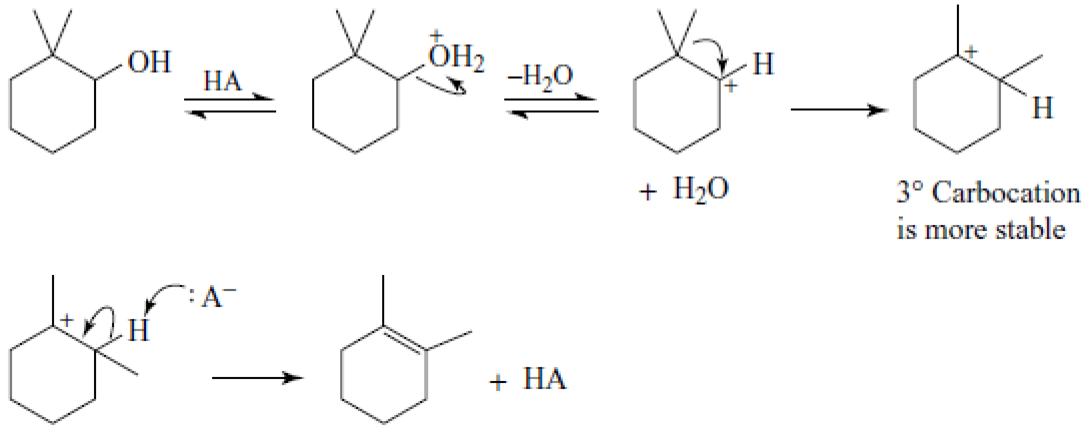
10.37



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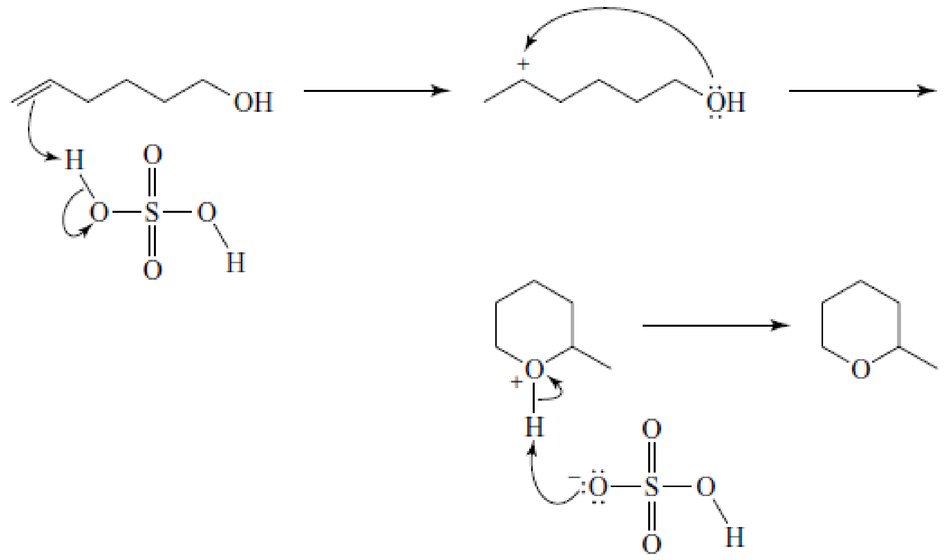

10.39

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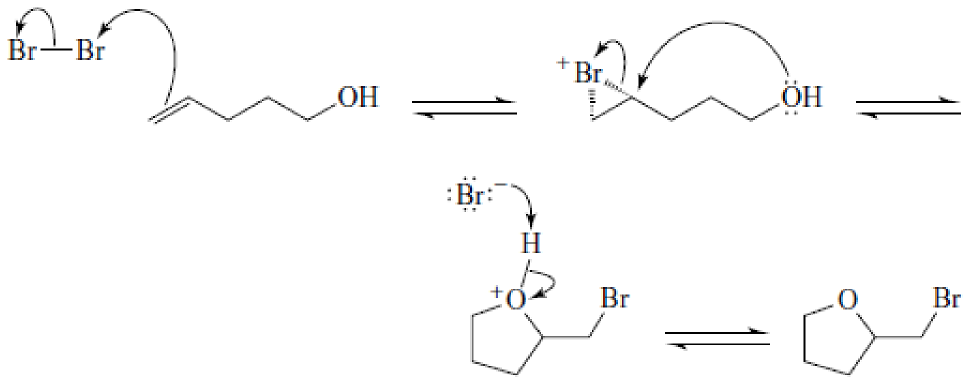

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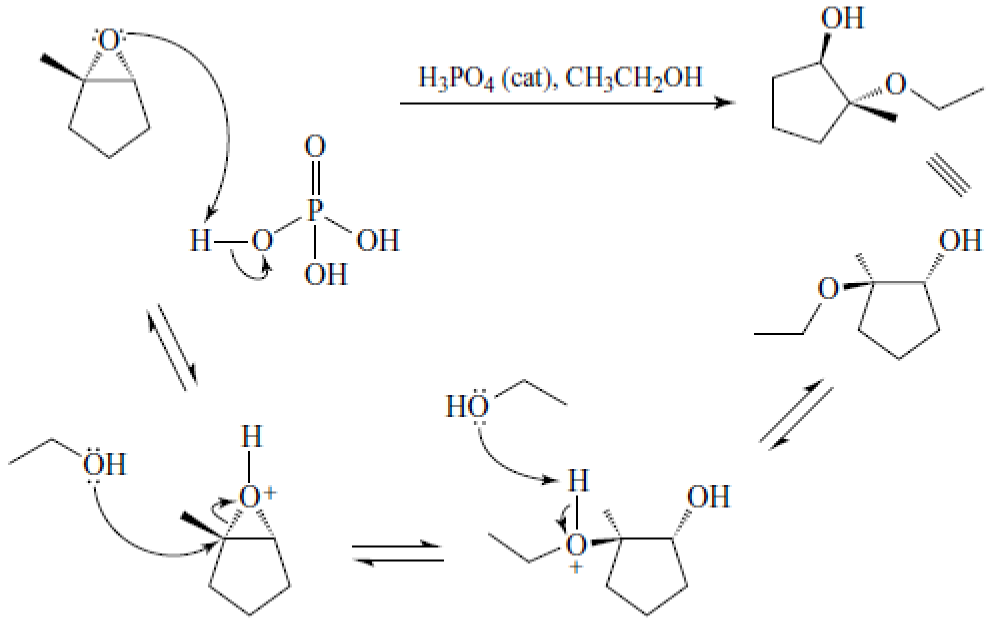

10.41

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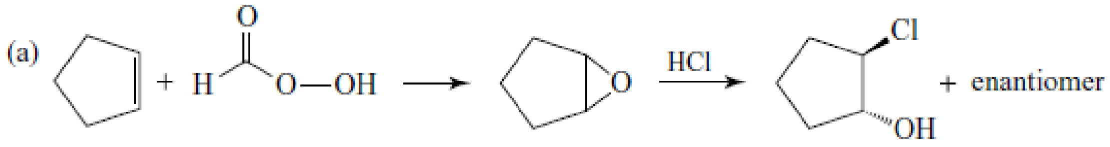
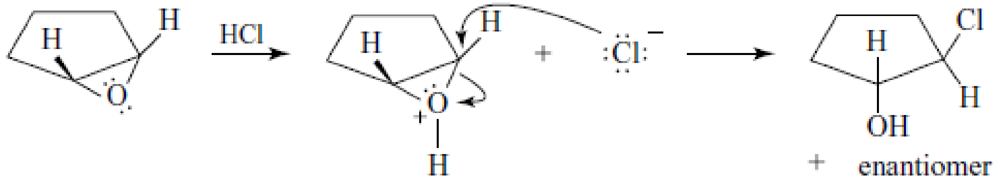


(b) The trans product because the Cl^- attacks anti to the epoxide and an inversion of configuration occurs.



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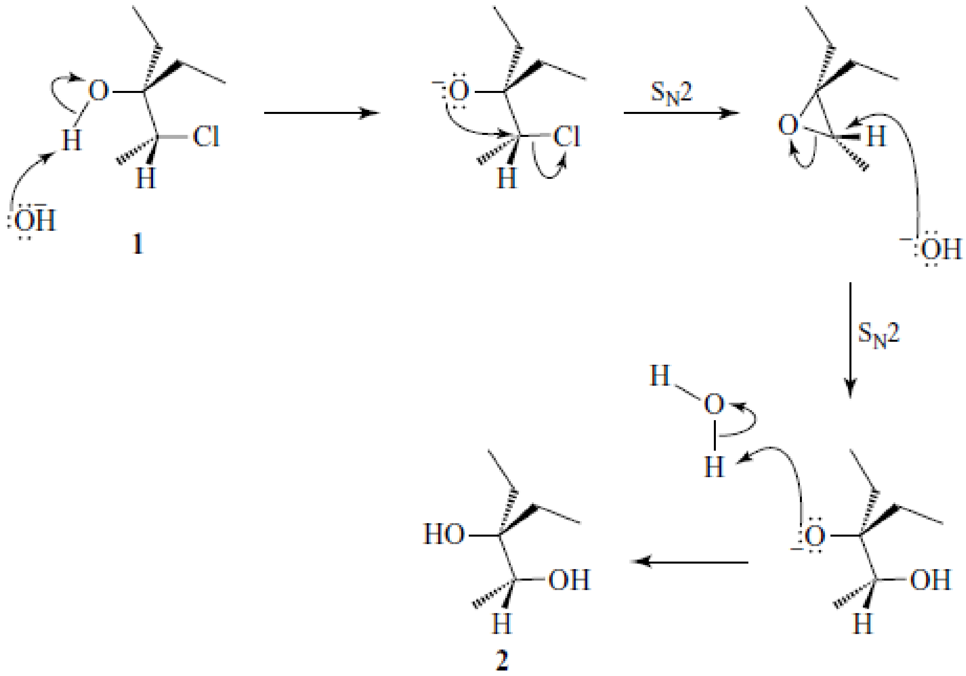

Two S_N2 reactions yield retention of configuration.

10.43

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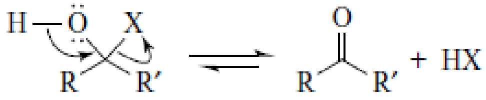
Collapse of the α-haloalcohol by loss of a proton and expulsion of a halide ion leads to the thermodynamically-favored carbonyl double bond. Practically speaking, the position of the following equilibrium is completely to the right.



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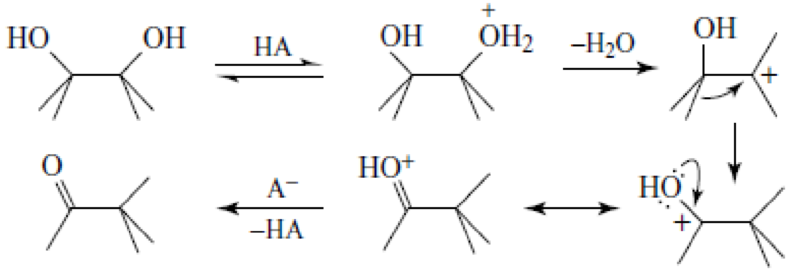

The reaction, known as the pinacol rearrangement, involves a 1,2-methanide shift to the positive center produced from the loss of the protonated —OH group.

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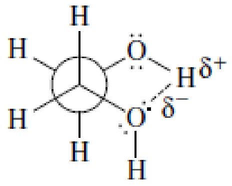
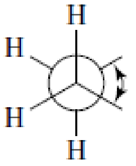
10.45

The angular methyl group impedes attack by the peroxy acid on the front of the molecule (as drawn in the problem). II results from epoxidation from the back of the molecule—the less hindered side.

10.46

For ethylene glycol, hydrogen bonding provides stabilization of the gauche conformer. This cannot occur in the case of gauche butane.





only van der Waals repulsive forces

<H1> **ADDITIONAL OBJECTIVE QUESTIONS**

<H2> **Single Correct Choice Type**

1. **(a)** Alkyl halide and phenol can be used. Aryl halide can't be used as it doesn't undergo substitution easily.
3. **(c)** Alkyl halide should be less sterically hindered.
4. **(a)** Phenoxide will attack alkyl halide to give substitution product.
5. (b) Ether is obtained alongside Silver halide.
6. (b) In Hydroboration Oxidation, addition of OH is as per anti-markovnikov product.
7. **(d)** One molecule of Grignard will first substitute alkoxy and then another will give addition.
8. **(b)** Mixed ether means that the alkyl groups on both sides of O are different.

9. **(a)** Addition of OH is as per Markovnikov rule in Oxymercuration Demercuration.
10. **(b)** X includes but-1-ene, cis-2-butene and trans-2-butene.
11. **(d)** Oxymercuration Demercuration reaction.
12. **(c)** Order of rate of reaction is as per the order of stability of carbocation.
13. (b) Formation of carbocation as per Markovnikov followed by rearrangement including hydride shift.
14. **(b)** Benzene will be formed when phenyl anion would abstract proton from the alcohol in an acid base reaction.
15. **(a)** Retention of configuration as the chiral carbon is not attacked. Hydride will abstract proton in first step and then alkoxide will attack as nucleophile and give substitution.
16. (a) Dehydration reaction.
17. **(c)** Both the O will be substituted with I due to excess HI.
18. (d) Q is propanal and S is propanone.
19. **(d)** Alkyl halide used should be less sterically hindered as it has to undergo nucleophilic substitution.
20. **(a)** Aryl carbocation is highly unstable, so it will not undergo hydrolysis.
21. **(d)** Williamson synthesis of ether is a nucleophilic substitution reaction.
22. **(a)** Addition is as per Markovnikov without rearrangement, while that in hydronium includes rearrangement with formation of sp^2 hybridised carbocation.
23. **(c)** Both the products would be formed by hydrolysis, one from each ring.
24. **(d)** Not isomers as ethyl group will be added to the alkoxide ion upon substitution.
25. **(b)** Alkyne is reduced to alkene in A and then in B, first the OH group on right is removed to form carbocation, which then undergoes resonance to yield the given product.
26. (a) Nucleophilic addition of Bromide ion will be from the opposite side.

<H2> **Linked Comprehension Type**

1. **(b)** D will be dehydration product. On reaction of D with Chromium complex, the aldehyde will be oxidized to carboxylic acid while the ketone will be unaffected. D can thus be arrived at by retrosynthetic analysis of the given molecule in ozonolysis reaction.

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2. **(a)** Reduction of C=O with LAH will result in the formation of alcohol which may be on the same side as the methyl groups or on opposite sides.
3. **(c)** B and C are geometrical isomers, thus diastereomers.
4. **(a)** A has keto group which is reduced with LAH.

<H2> Integer Type

1. **(3)** One mole each will be consumed by the alcohol, alkene and the methoxy ether.

<H2> Matrix Match Type

1. a→(p); b→(s); c→(q); d→(r)

It is Hydroboration Oxidation reaction.

2. a→(q); b→(s); c→(r); d→(p)

HIO_4 results in oxidation by cleavage of the C-C bond of vicinal diol.

3. a→(s); b→(r); c→(q); d→(p)

Option (a): OH will be removed as water and methoxy group will substitute it.

Option (b): NaH will abstract proton from alcohol and the alkoxide will then give nucleophilic substitution.

Option (c): Br will substitute OH, then Grignard will form which will then give nucleophilic substitution with methyl iodide.

Option (d): Na (active metal) will remove proton to yield alkoxide which will act as nucleophile.

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Chapter 11: Alcohols from Carbonyl Compounds

Practice Problems

11.1

(a) $LiAlH_4$

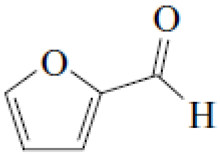
(b) $LiAlH_4$

(c) $NaBH_4$

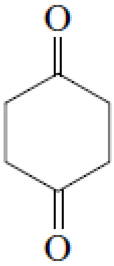
(d) $LiAlH_4$

(e) $LiAlH_4$

11.2

(a) 

(b) No reaction. Ethers can not be oxidized.

(c) 

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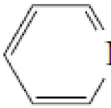
(a)  $\overset{+}{N}H$ CrO_3Cl^- (PCC)/CH_2Cl_2 or $\xrightarrow[\text{(2) } Et_3N]{\text{(1) DMSO, } (COCl)_2, -60\ ^\circ C}$

(b) $KMnO_4$, HO^-, H_2O, heat; then H_3O^+ [or conditions as in (c) below]

(c) H_2CrO_4/acetone [or conditions as in (b) above], or Swern oxidation

(d) (1) O_3 (2) Me_2S

(e) $LiAlH_4$

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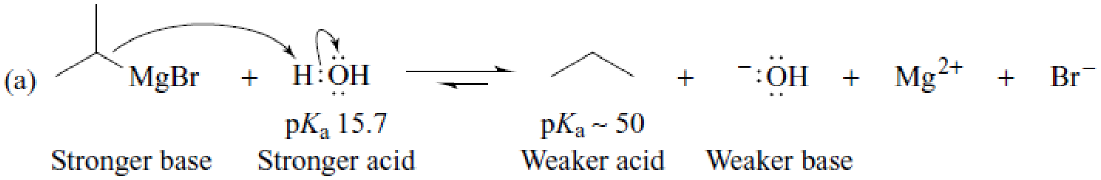
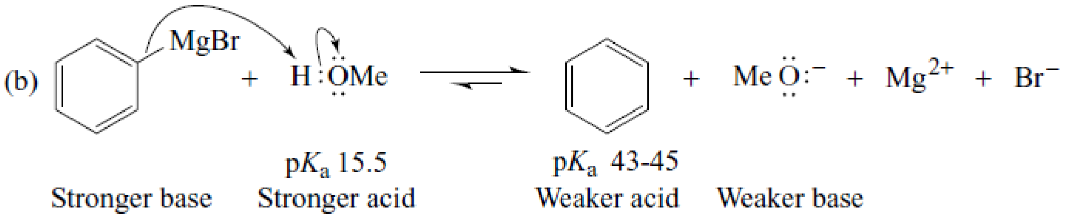
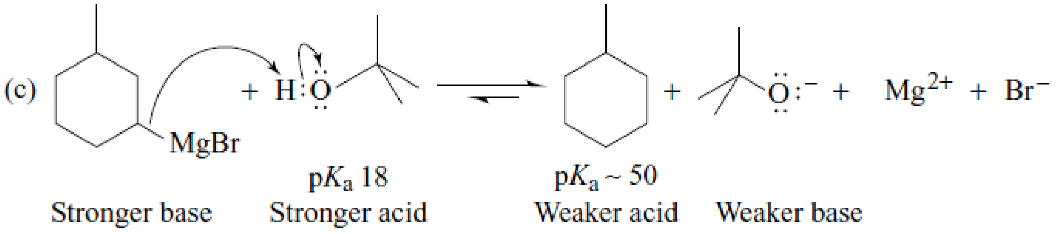
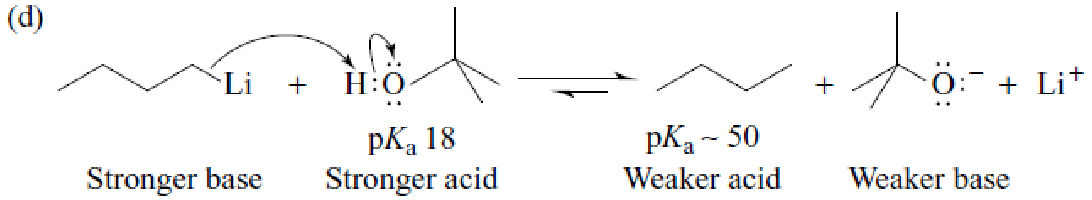
11.4









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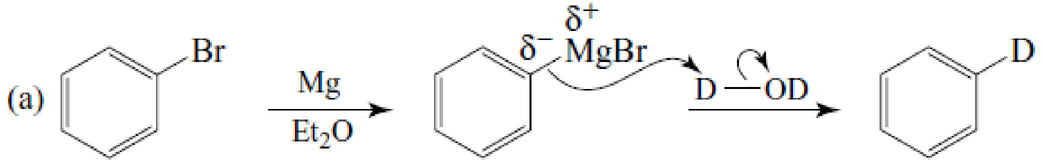

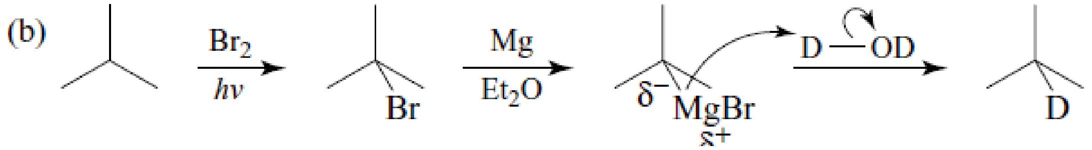

11.6

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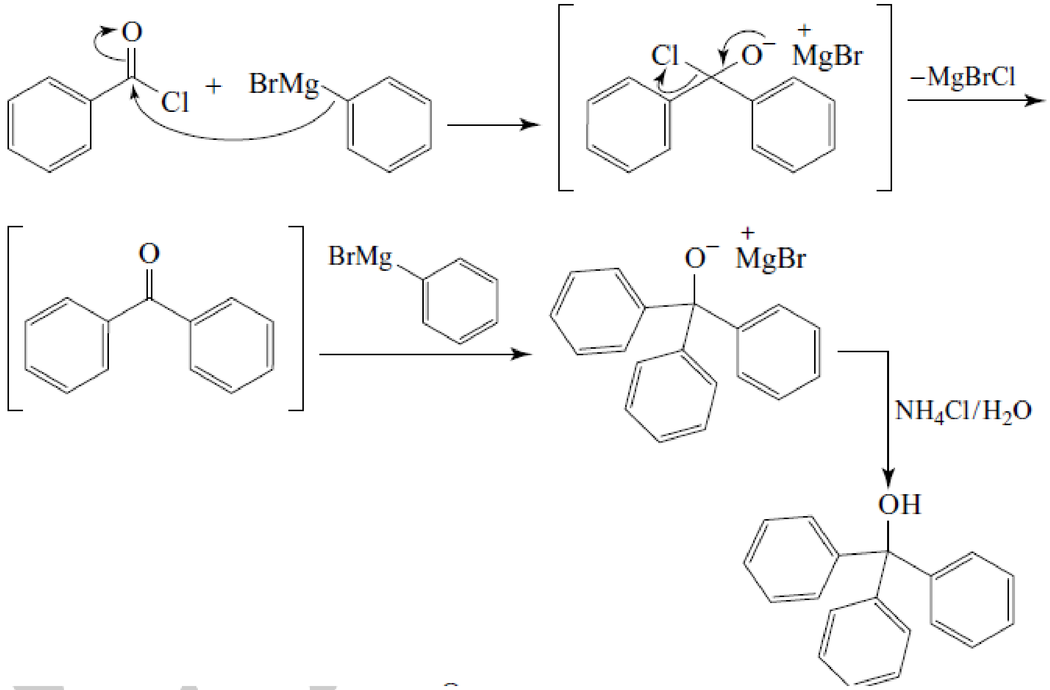

11.7

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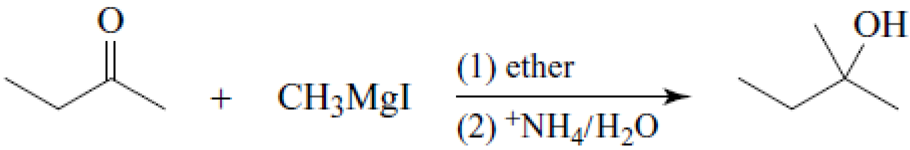

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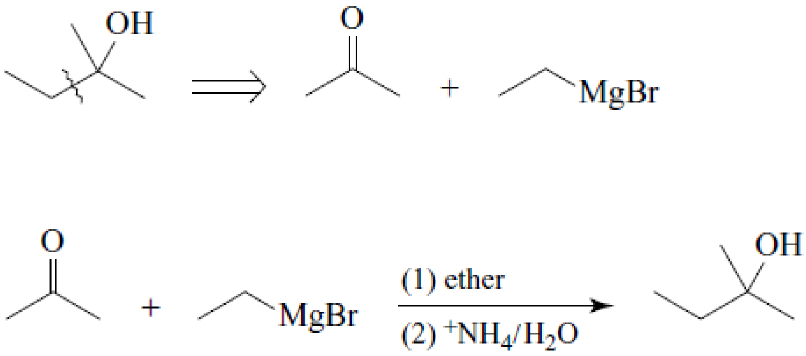

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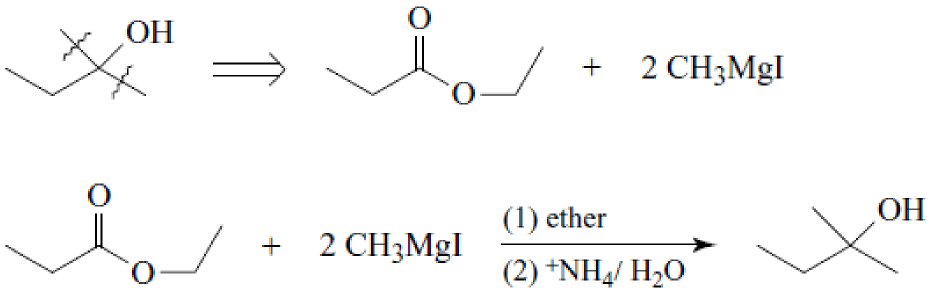

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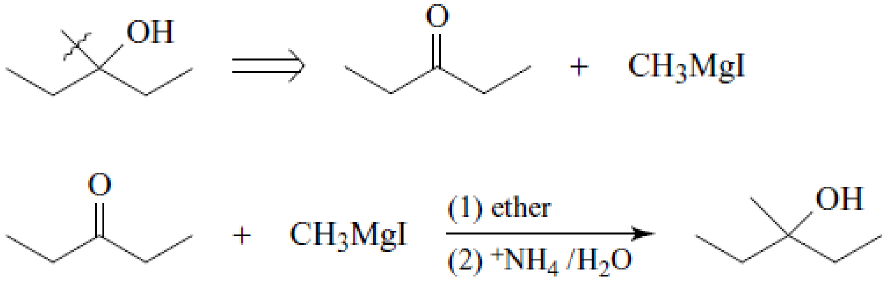

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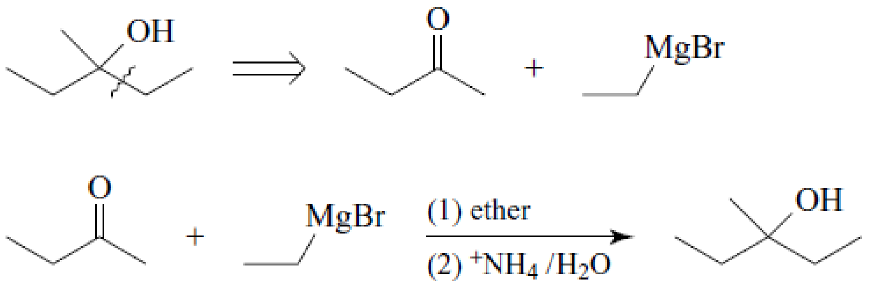

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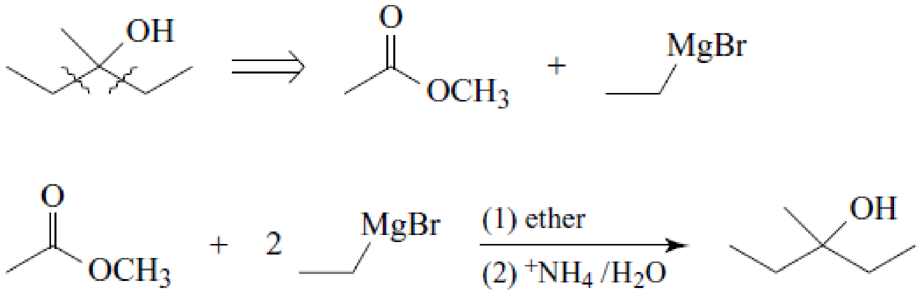

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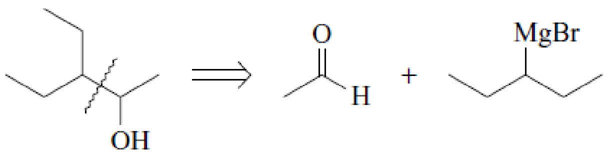

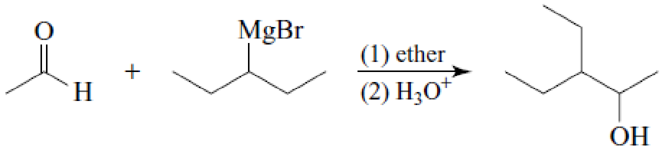

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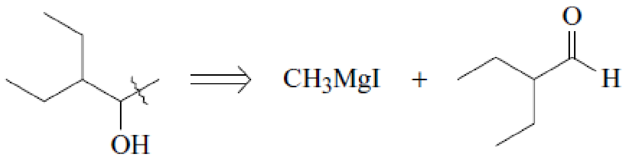

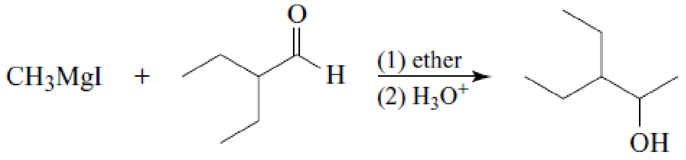

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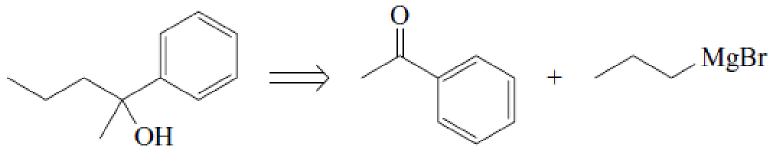

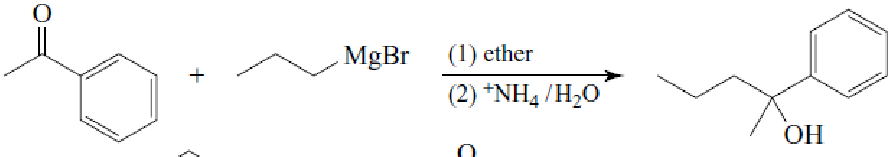

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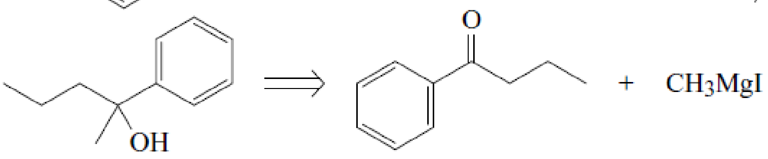

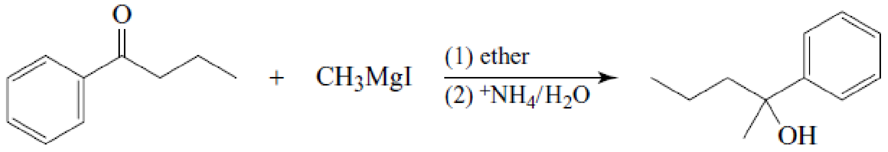

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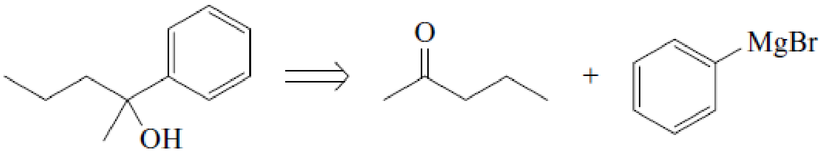
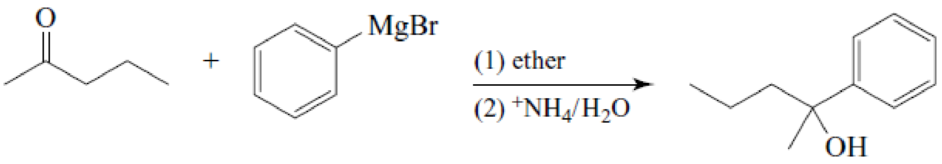
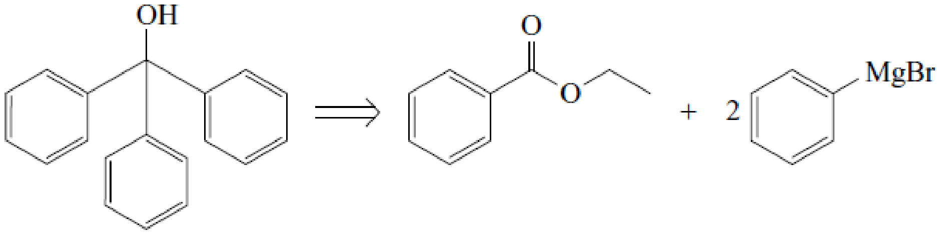
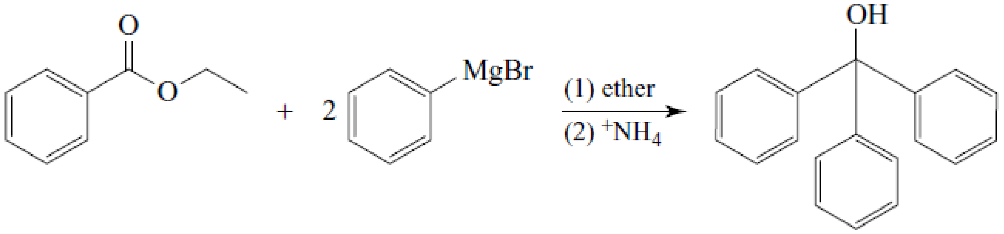
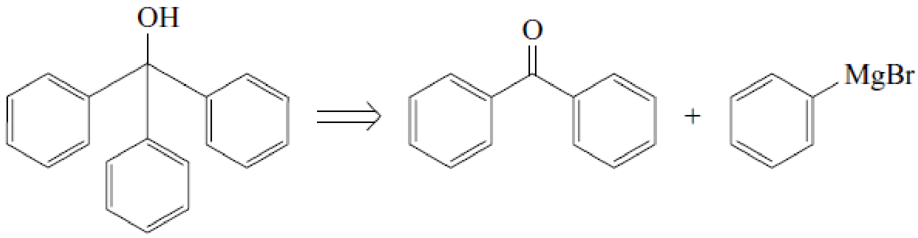
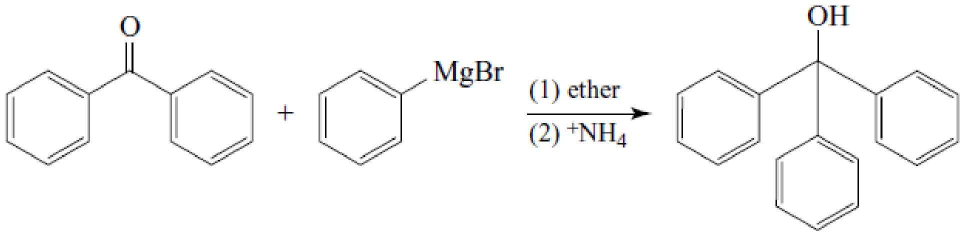
(3) 



(e) (1) 



(2) 



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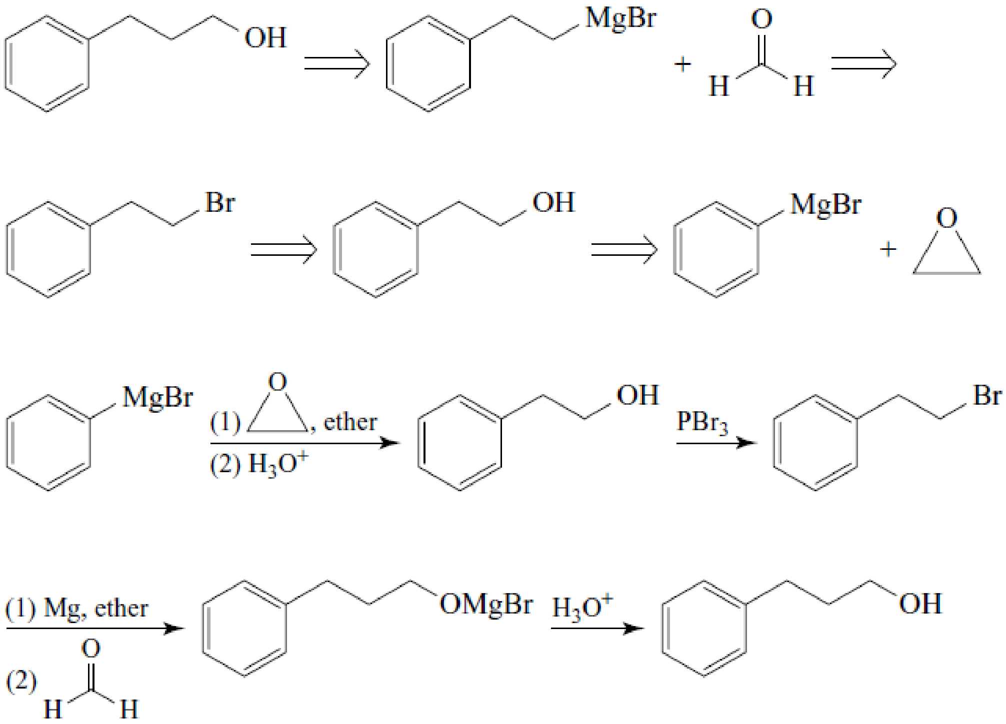

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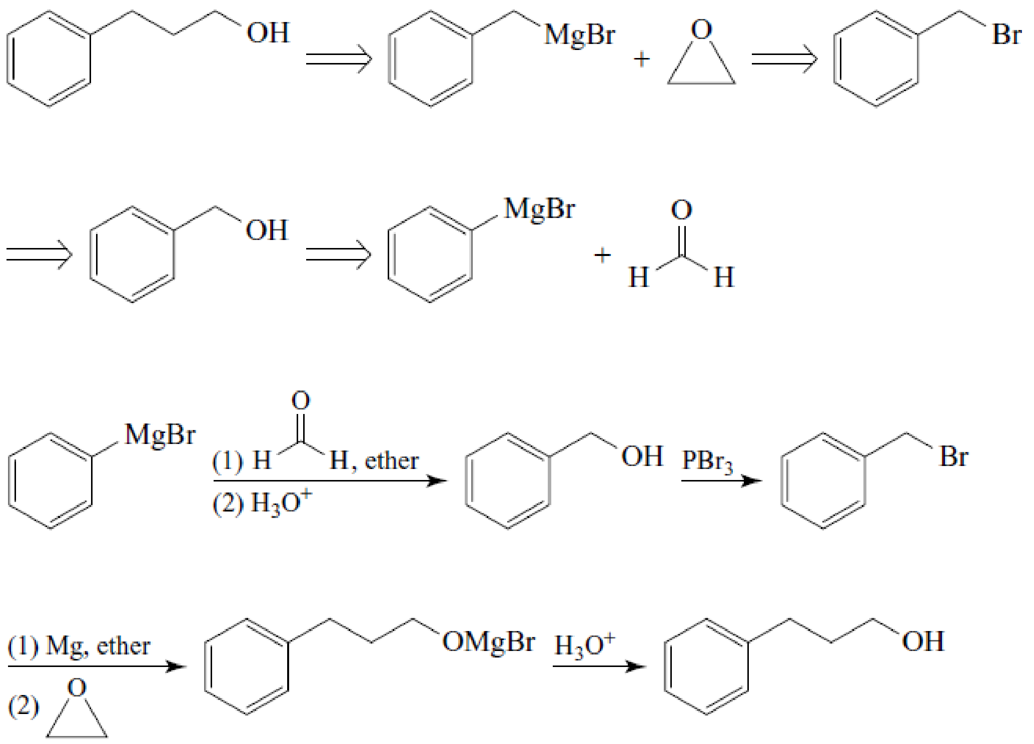

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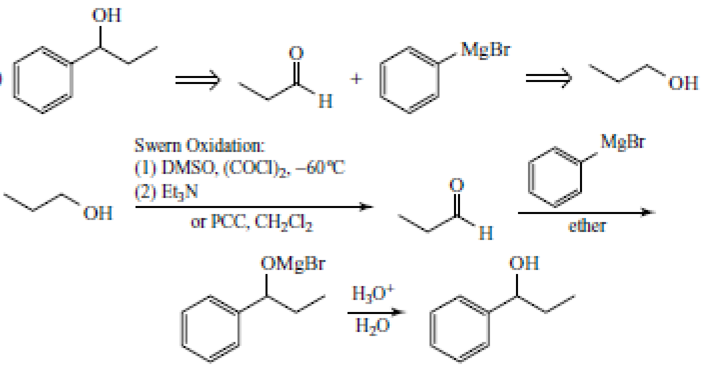

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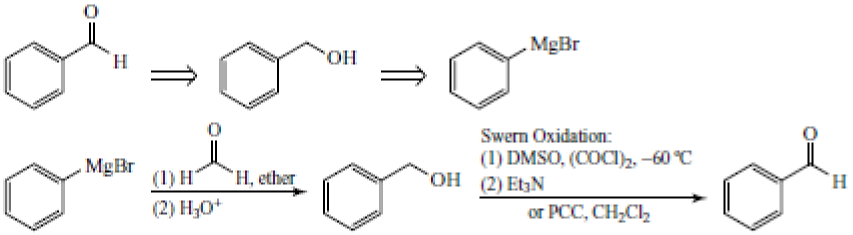

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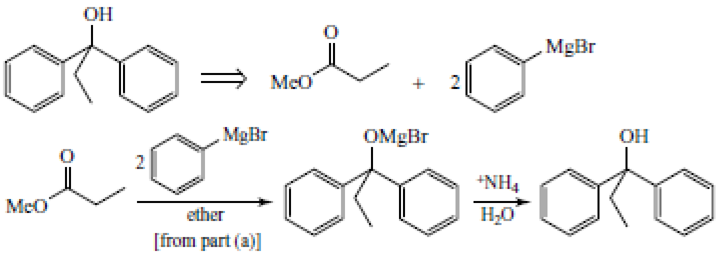

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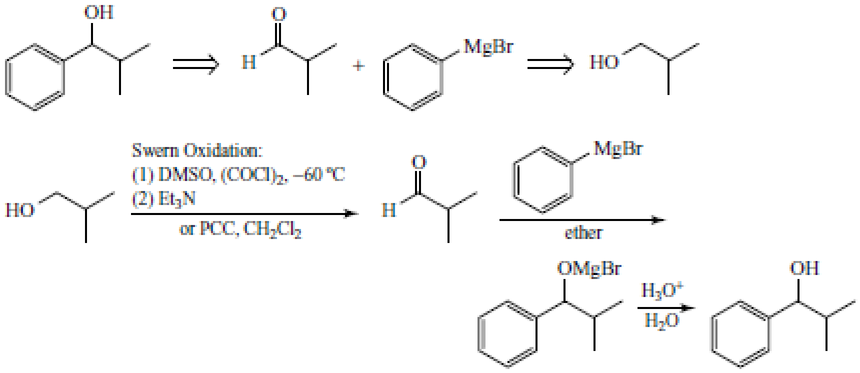

Review Problems

<H1> ADDITIONAL OBJECTIVE QUESTIONS

Reagents and Reactions

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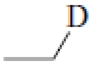
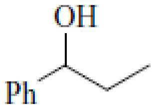
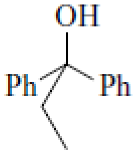
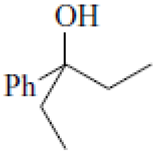
11.9

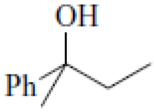
(a) CH_3CH_3

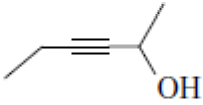
(b) 

(c) 

(d) 

(e) 

(f) 

(g) CH_3CH_3 + 

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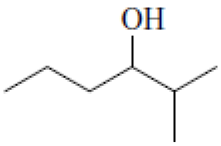
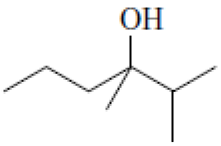
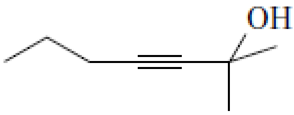
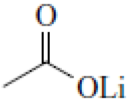
(a) 

(b) 

(c) + 

(d) +

(e)

+ 

11.11

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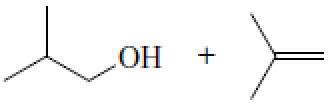
(a) 

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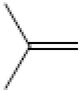
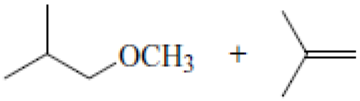
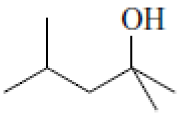
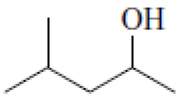
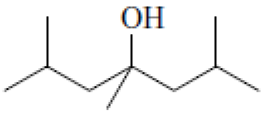
(c) 

(d) 

(e) 

(f) 

(g) 

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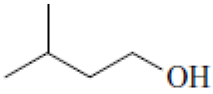
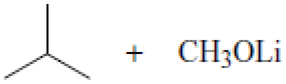
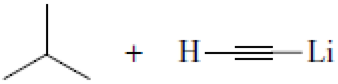
(i) 

(j) 

(k) 

11.12

(a) $LiAlH_4$

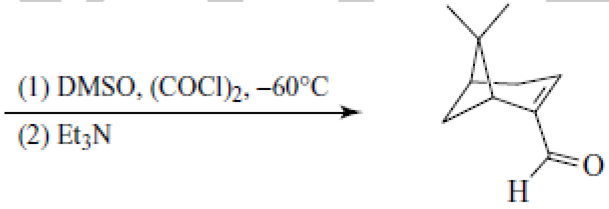
(b) $NaBH_4$

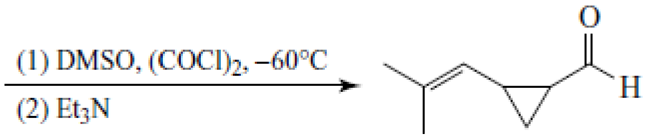
(c) $LiAlH_4$

(d) (1) $KMnO_4$, HO^-, heat (2) H_3O^+ (or H_2CrO_4/acetone)

(e) PCC/CH_2Cl_2 or Swern oxidation

11.13

(a) Myrtenol 

(b) Chrysanthemyl alcohol 

11.14

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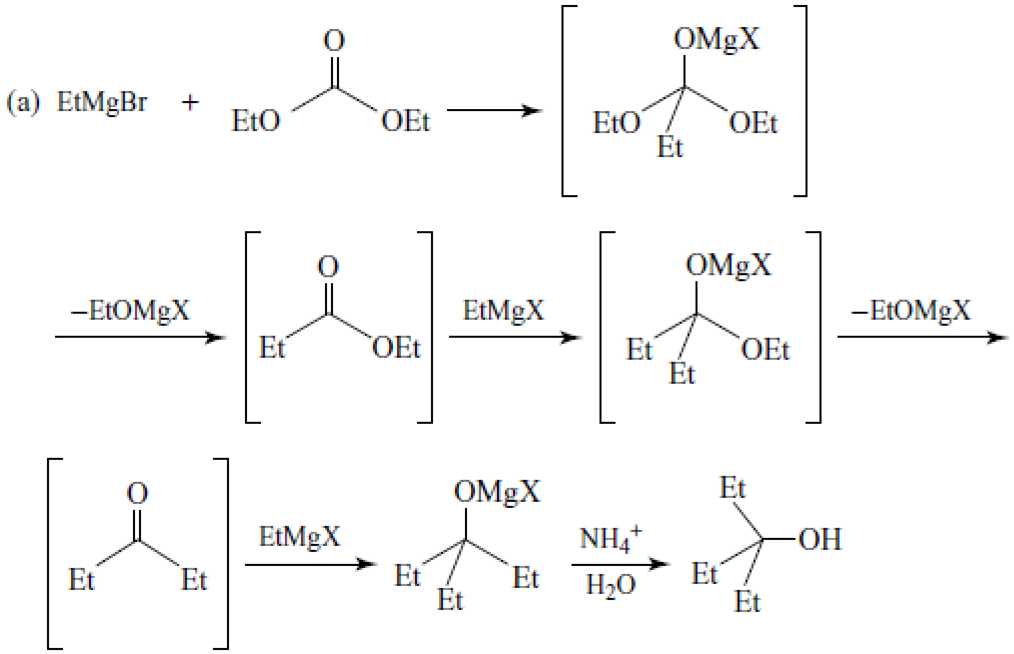

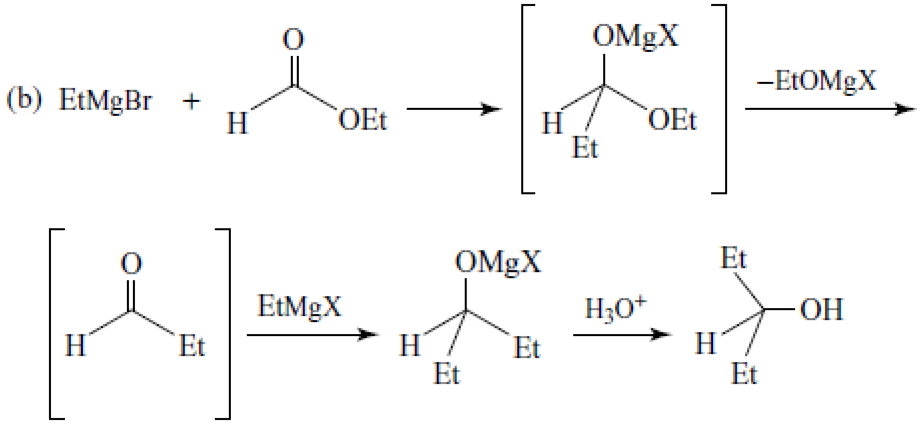

11.15

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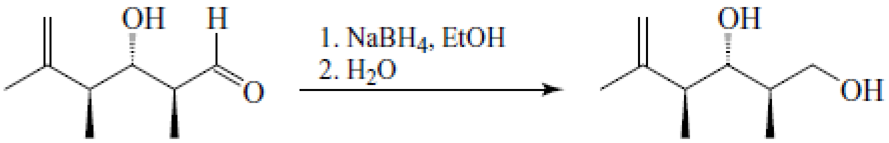
(a)



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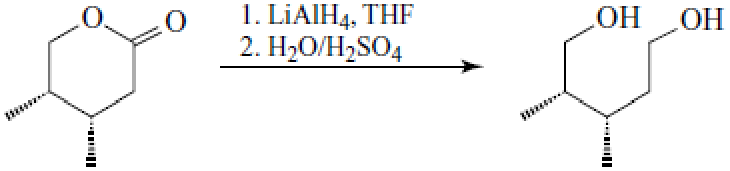

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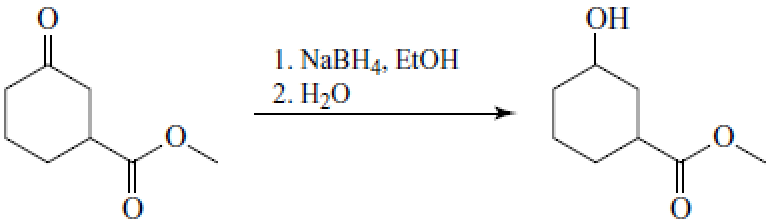

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11.16

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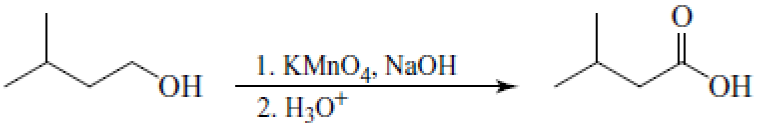
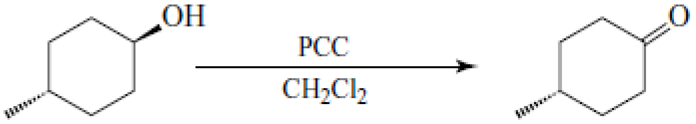
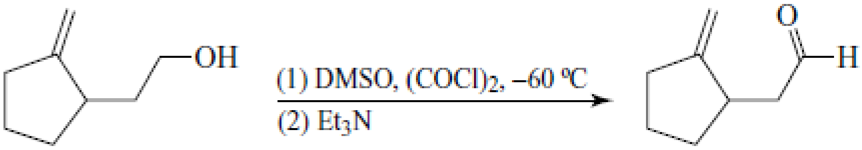
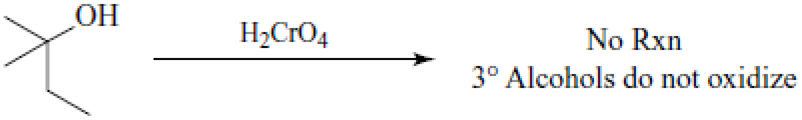
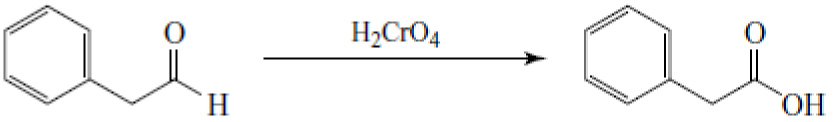
(a) 

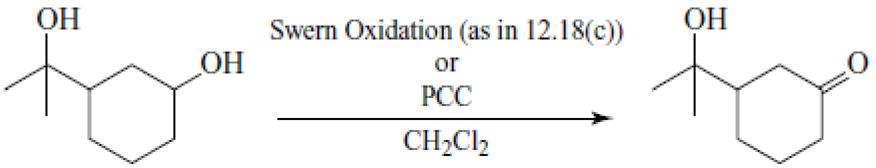
(b) 

(c) 

(d) 

(e) 

11.17

(a) 

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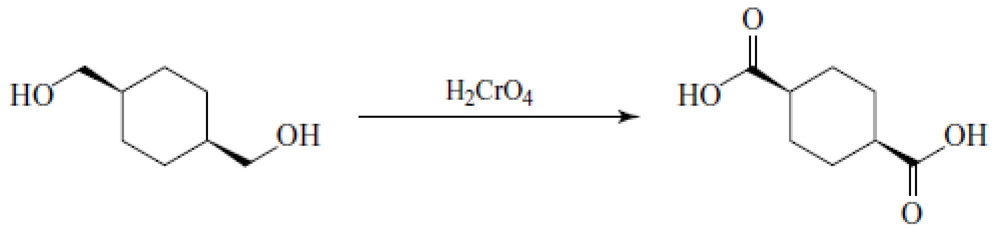

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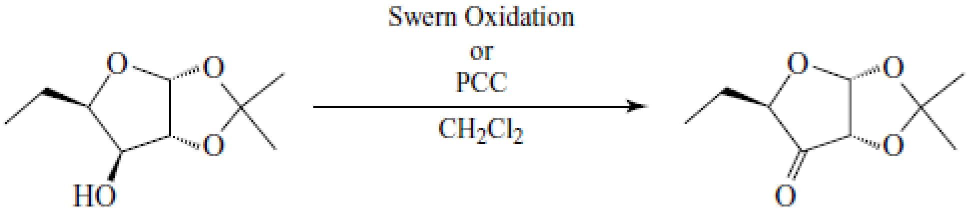

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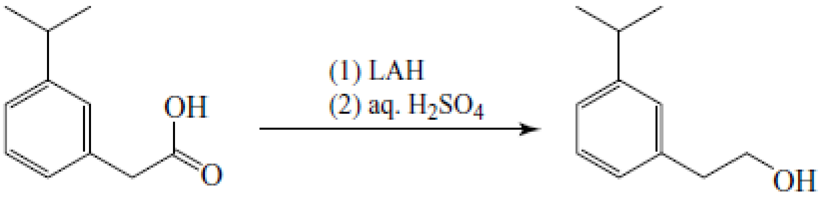

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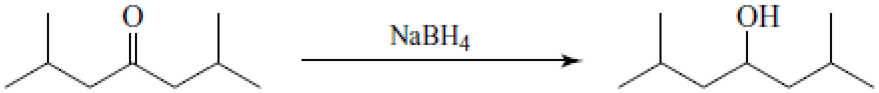

11.18

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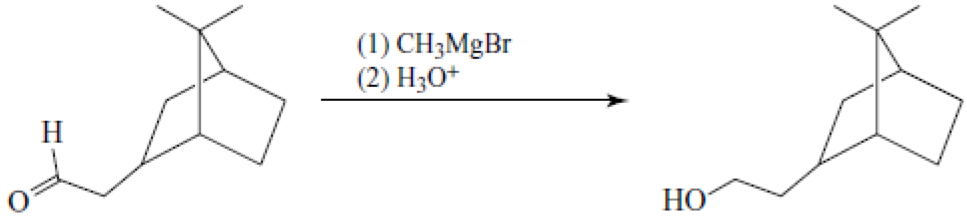
(a)



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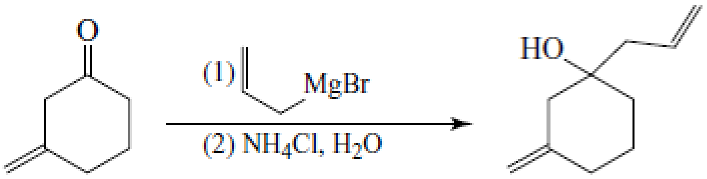

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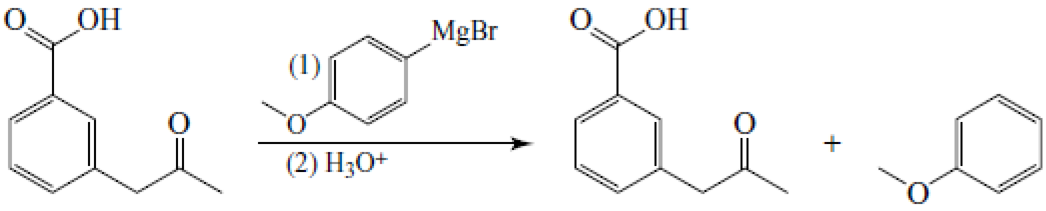

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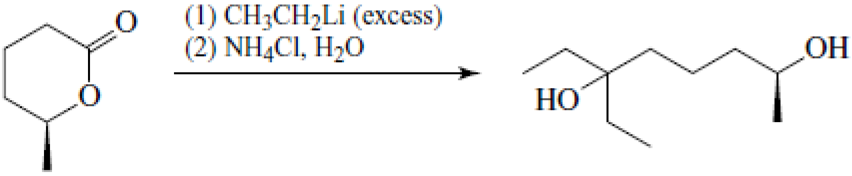

11.19

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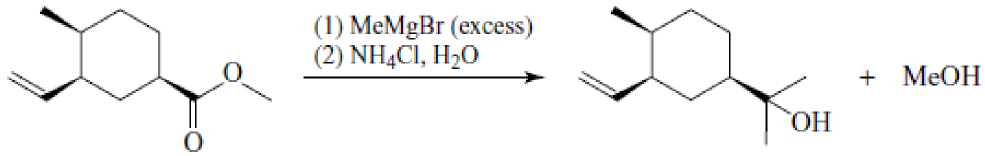
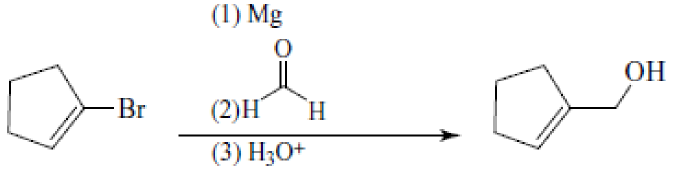
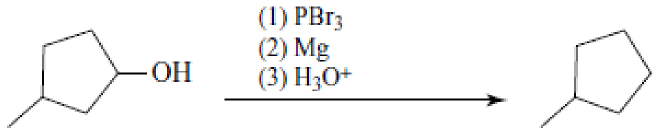
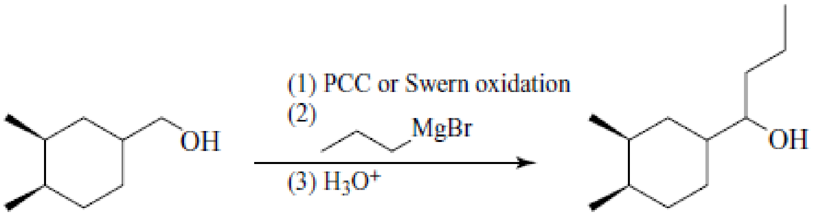
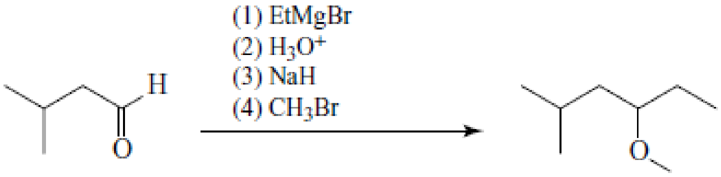
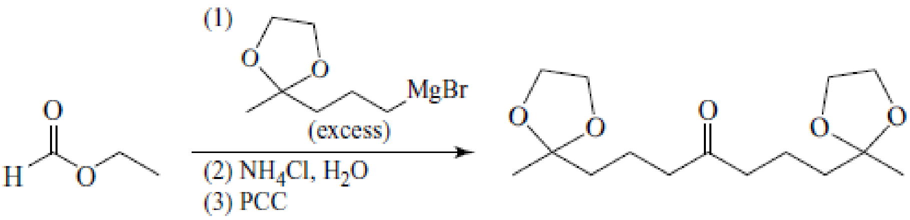
(a) 

(b) 

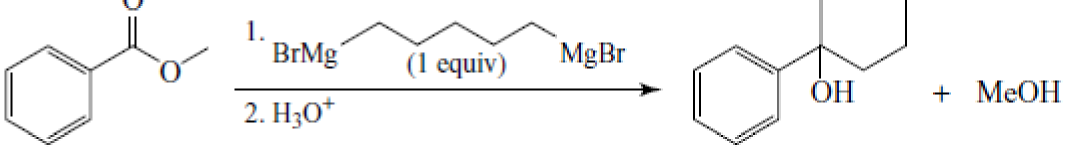
(c) 

(d) 

(e) 

(f) 

11.20



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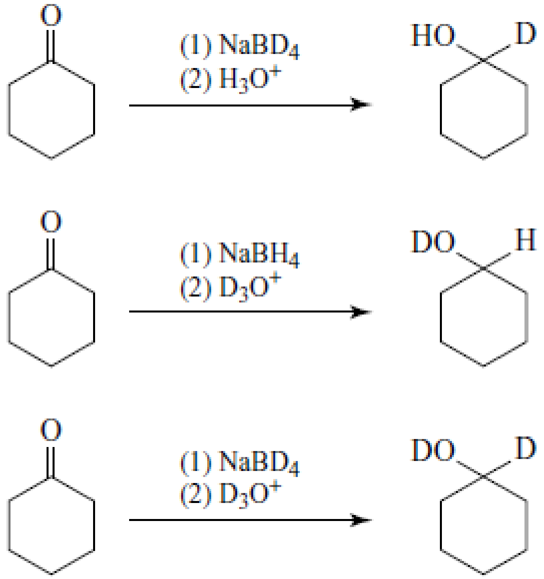
Mechanisms

11.21



11.24

The three- and four-membered rings are strained, and so they open on reaction with RMgX or RLi. THF possesses an essentially unstrained ring and hence is far more resistant to attack by an organometallic compound.

Synthesis

11.25

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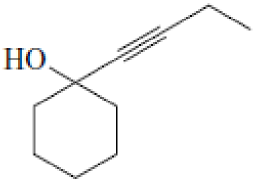
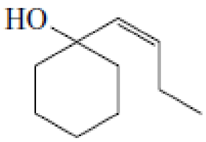
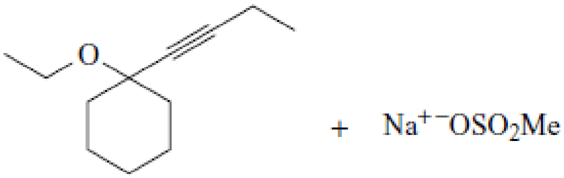
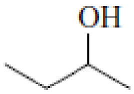
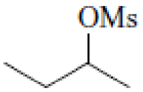
(a)

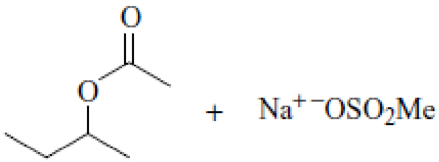
(b) 

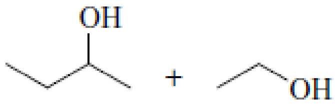
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

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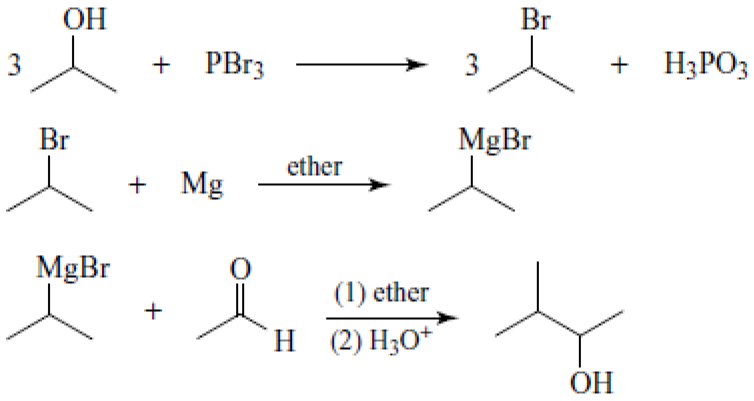
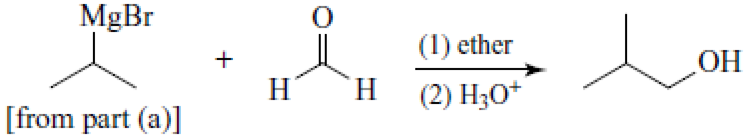
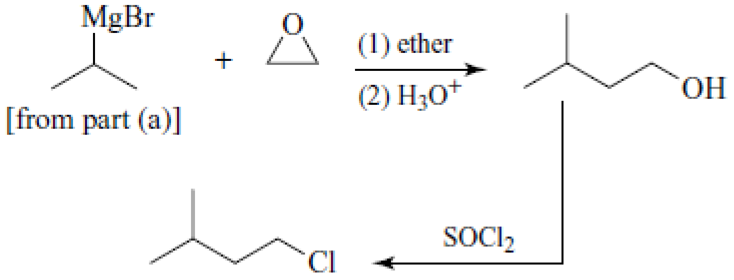
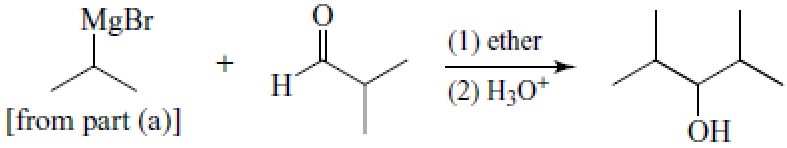
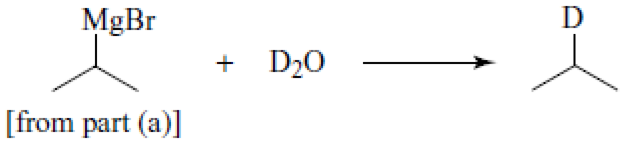
11.26

(a) 

(b) 

(c) 

(d) 

(e) 

11.27

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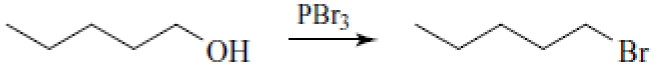
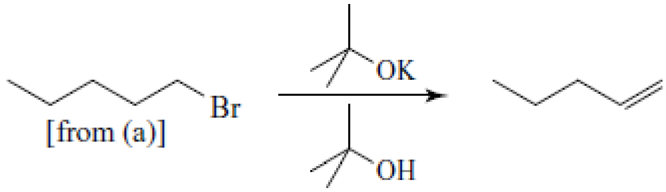
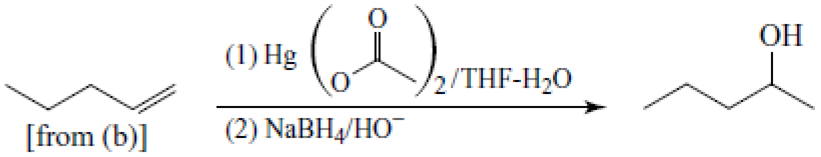
(a) 

(b) 

(c) 

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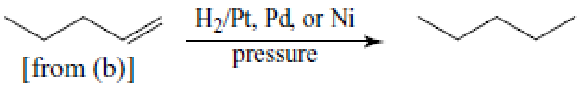
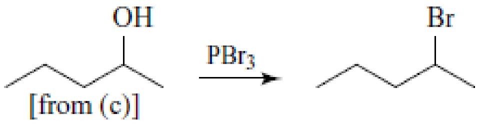
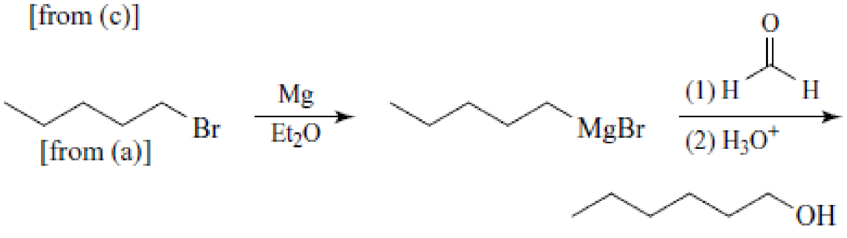
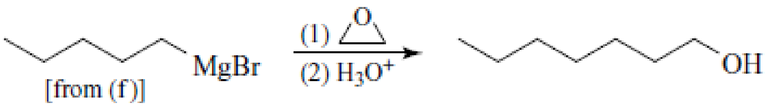
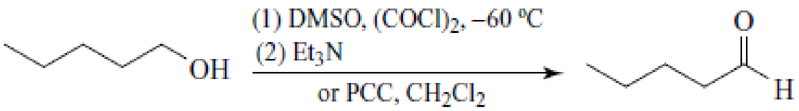
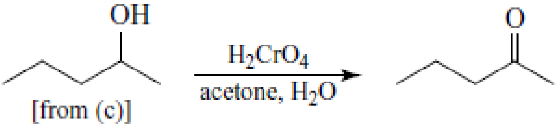
(d) 

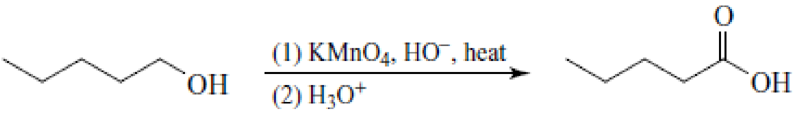
(e) 

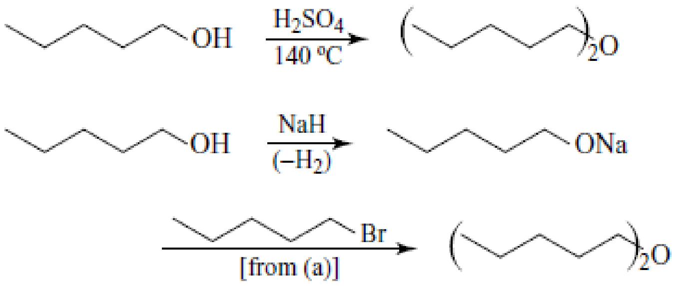
(f) 

(g) 

(h) 

(i) 

(j) 

(k) (1) 

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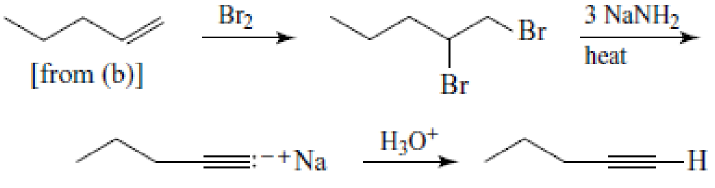
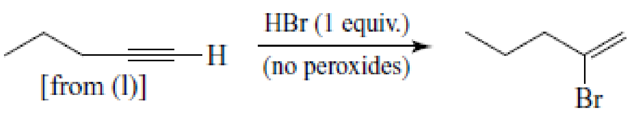
(l) 

(m) 

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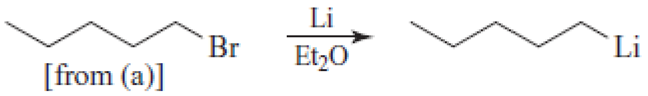
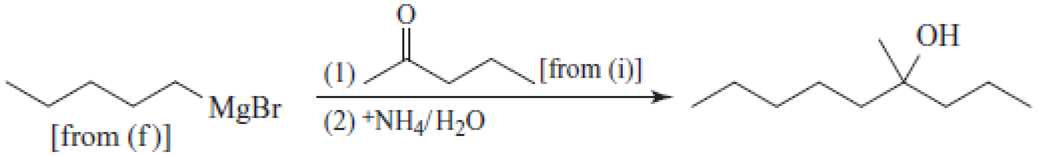
(n) 

(o) 

11.28

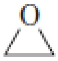
(a) $NaBH_4$, ^{-}OH

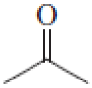
(b) 85% H_3PO_4, heat

(c) H_2/Ni_2B (P-2)

(d) (1) BH_3:THF
(2) H_2O_2, ^{-}OH

(e) (1) NaH (2) $(CH_3)_2SO_4$

(f) (1) PBr_3 (2) Mg (3)  (4) HA

(g) (1) CH_3MgBr/Et_2O
(2) 
(3) NH_4Cl/H_2O

11.29

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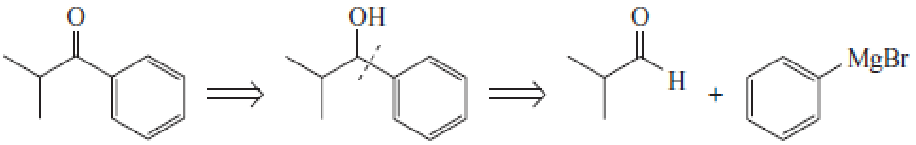
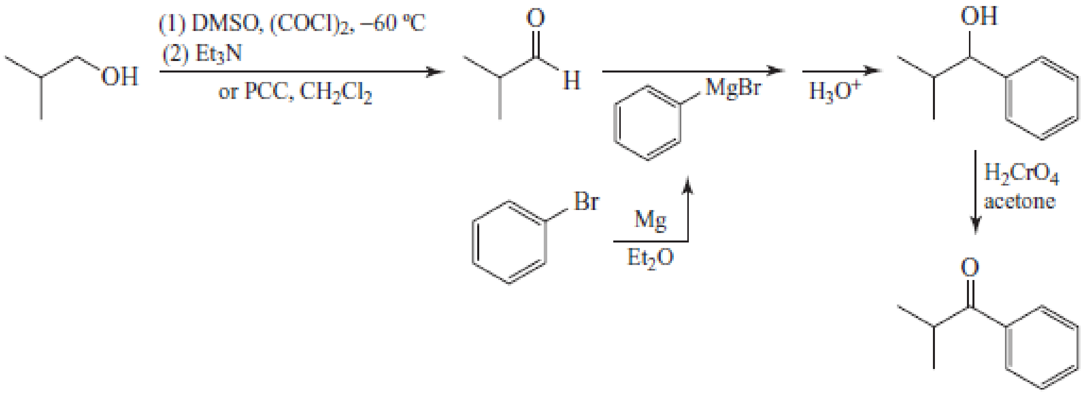
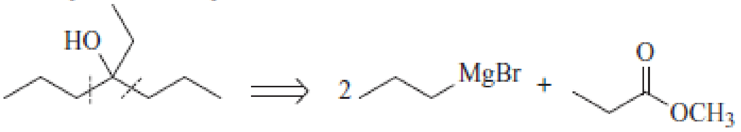
(a) ***Retrosynthetic Analysis***



Synthesis



(b) ***Retrosynthetic Analysis***



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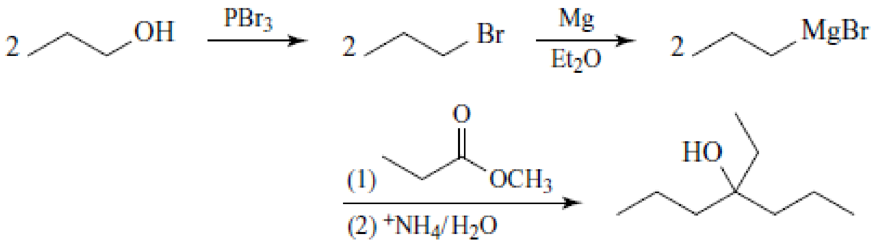
Synthesis



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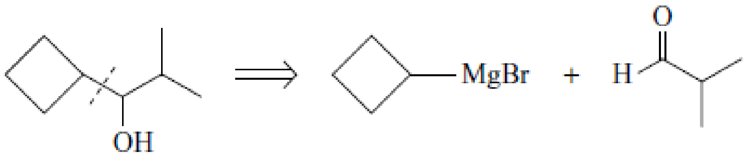

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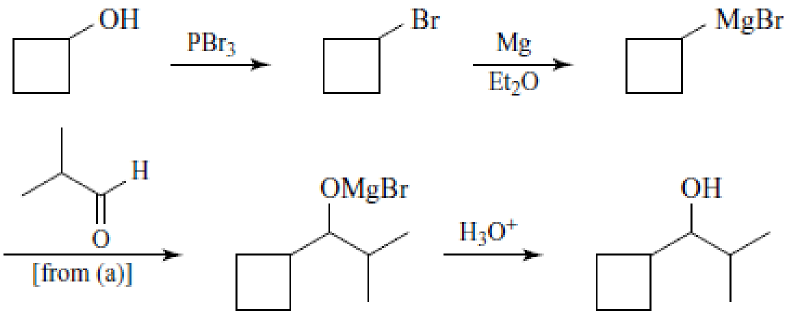
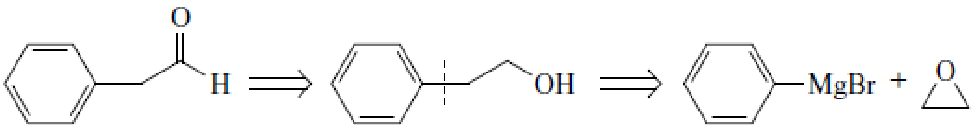


(d) ***Retrosynthetic Analysis***



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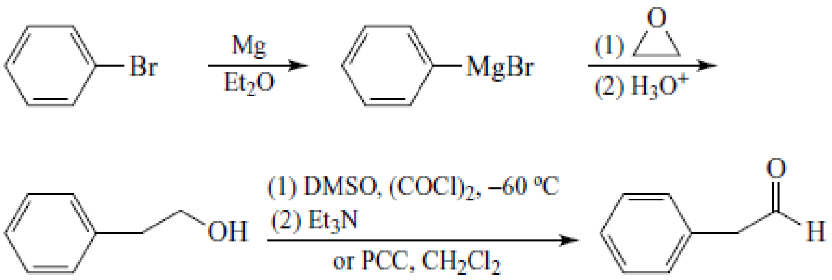
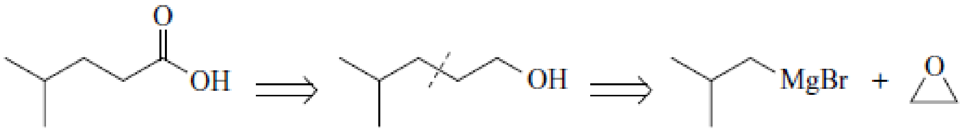


(e) ***Retrosynthetic Analysis***



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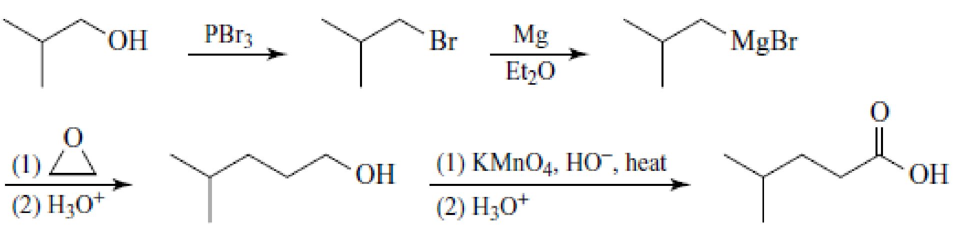
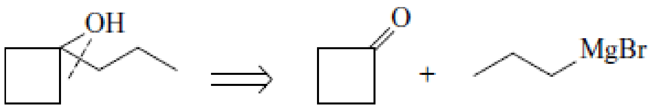
Synthesis



(f) ***Retrosynthetic Analysis***



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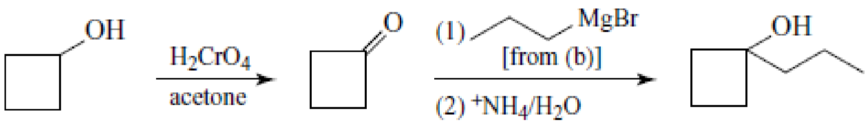
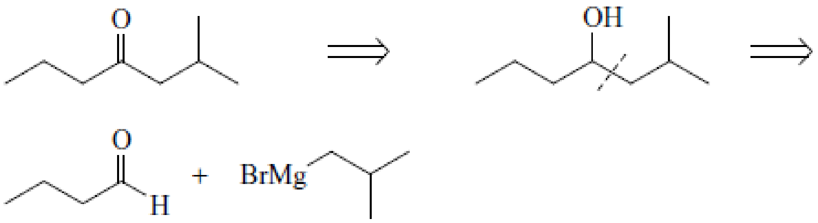
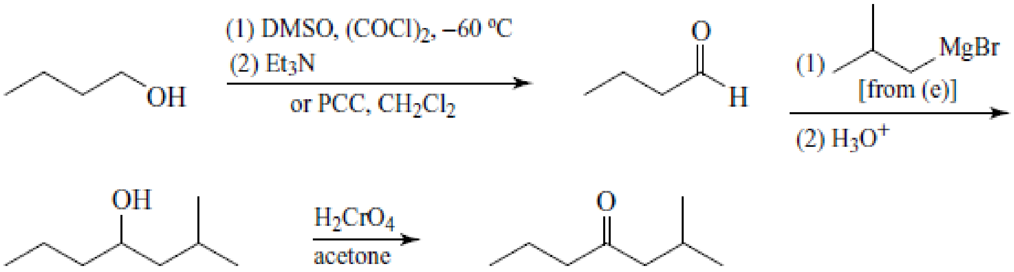


(g) ***Retrosynthetic Analysis***



Synthesis



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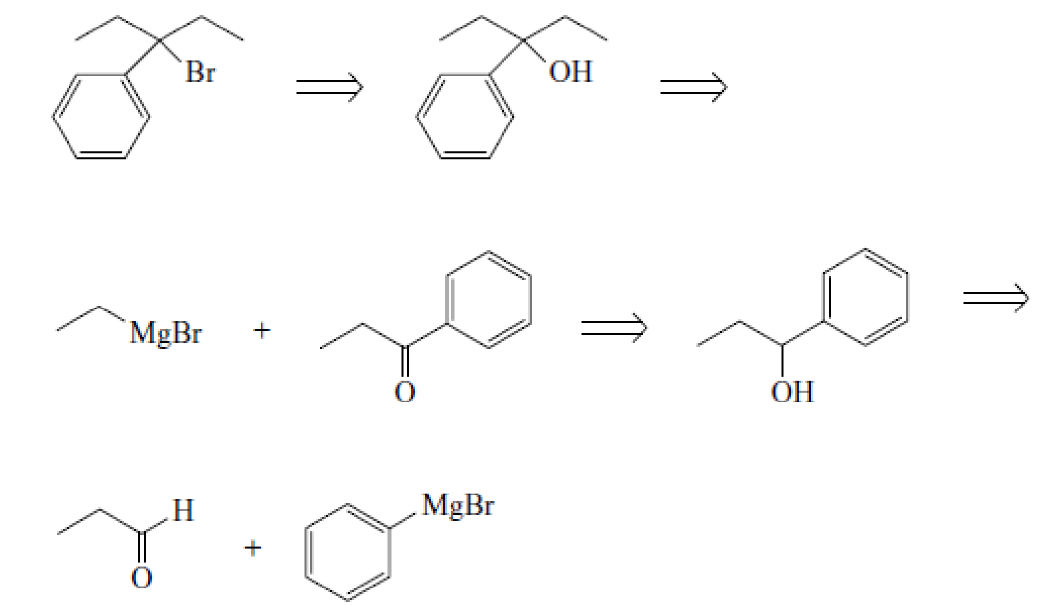
(h) ***Retrosynthetic Analysis***



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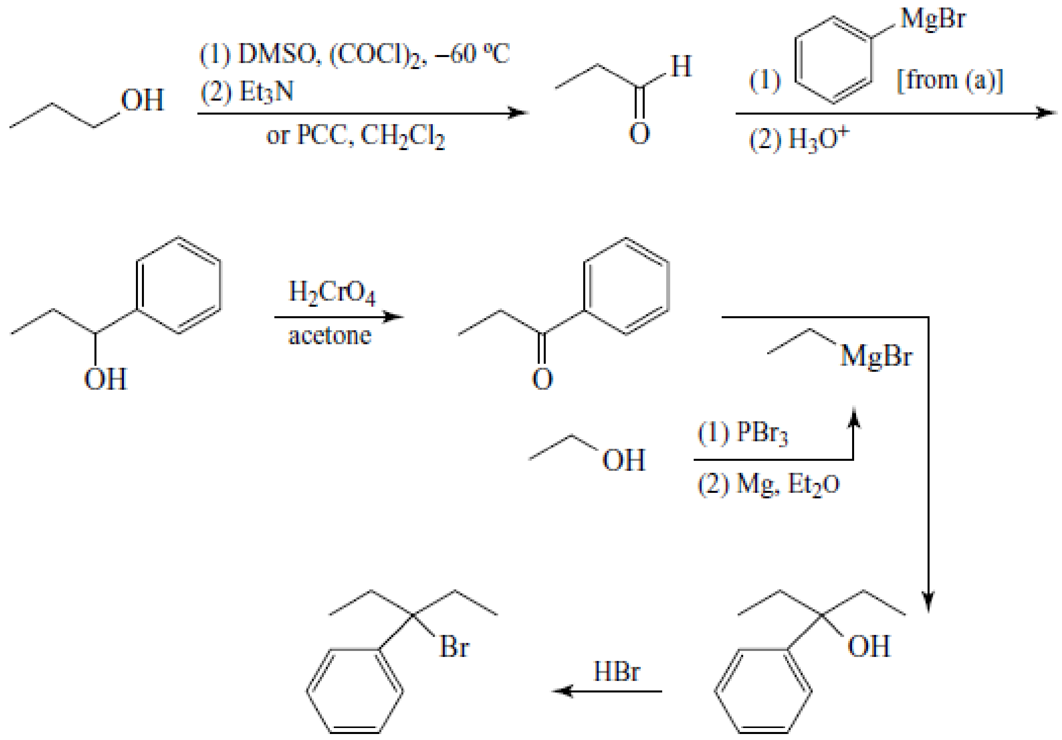

11.30

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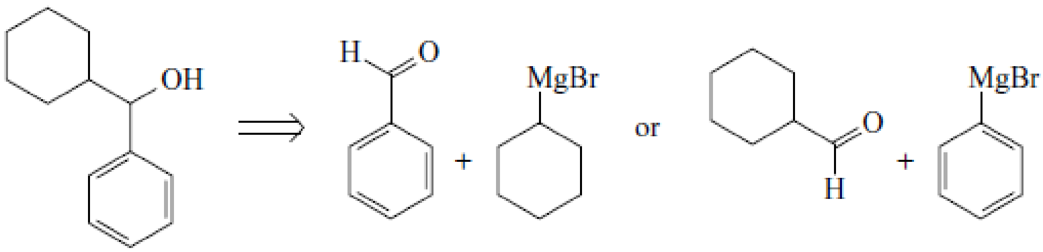
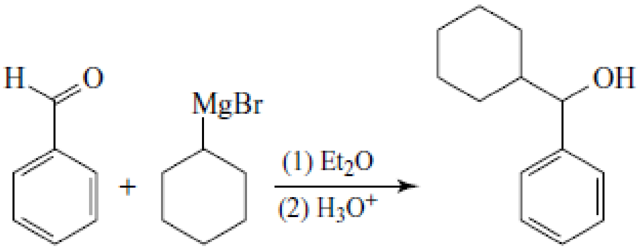
(a)





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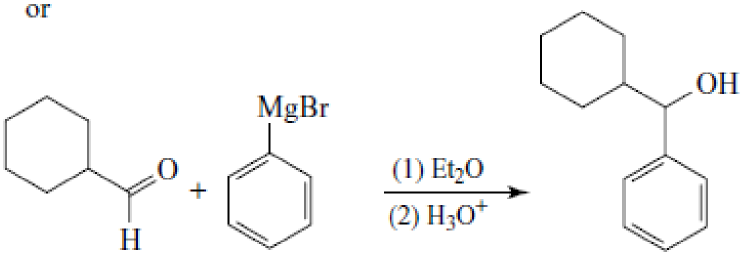

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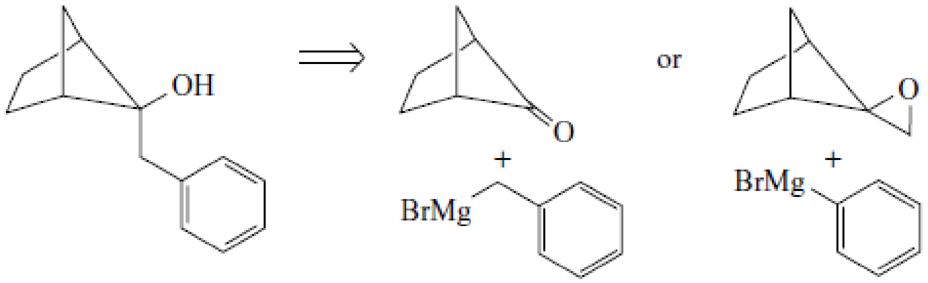

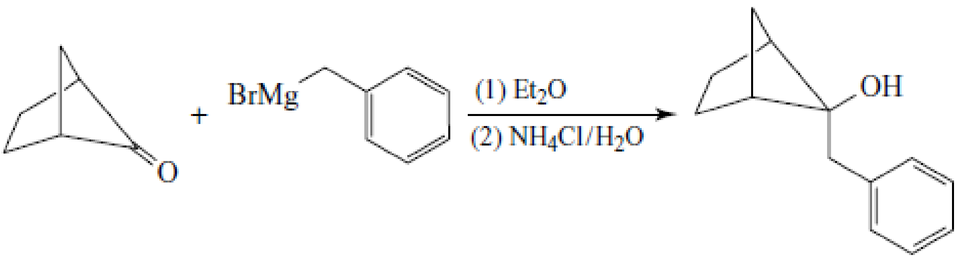

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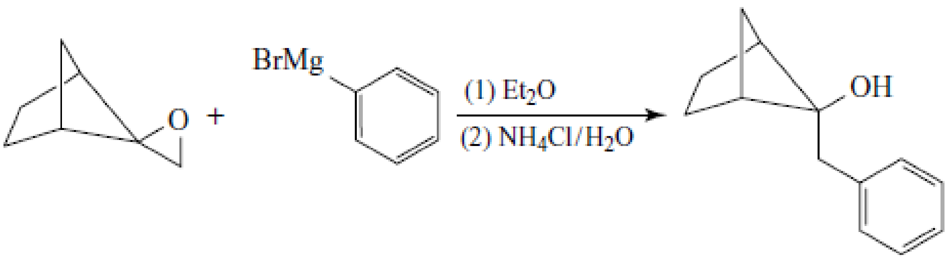

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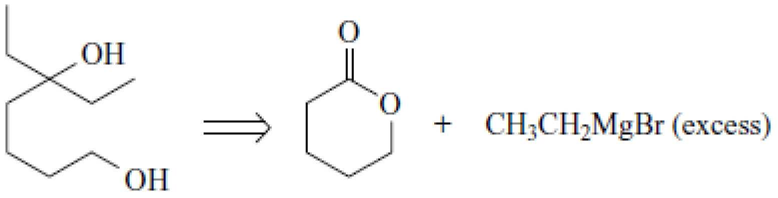
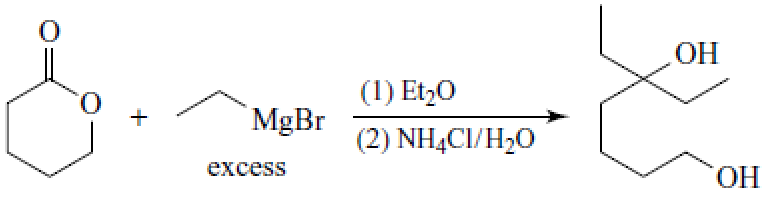
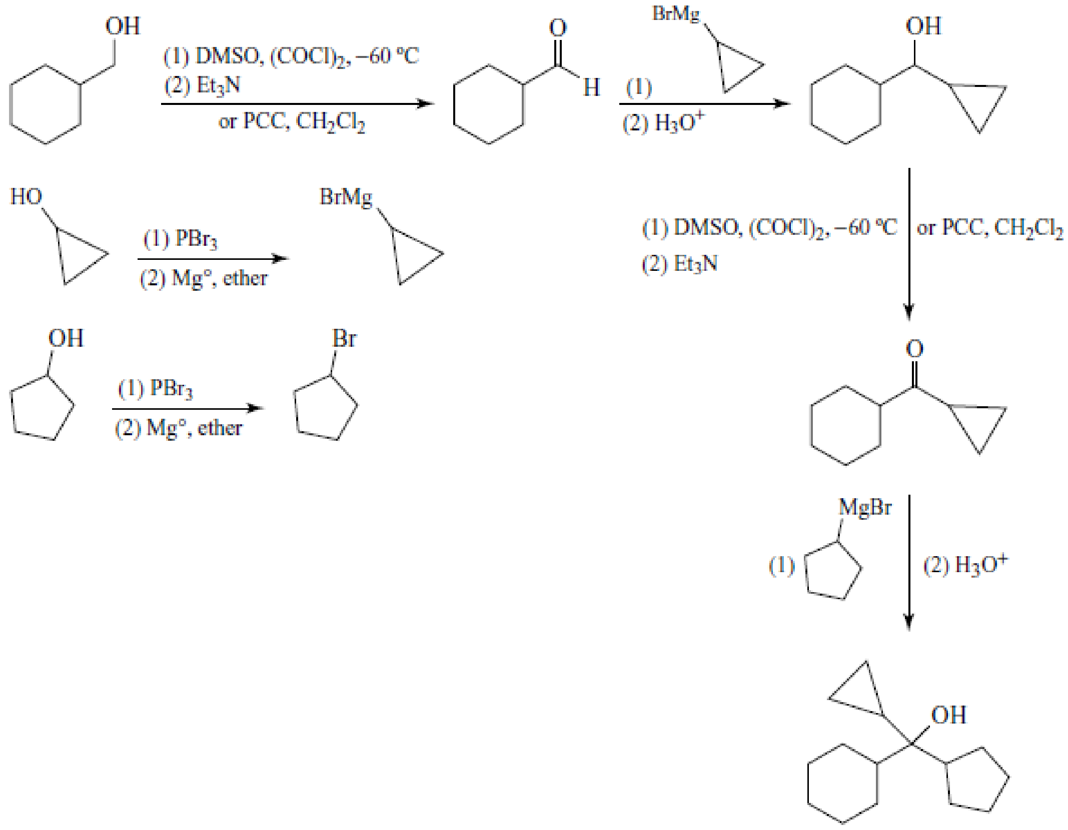




11.31

There are multiple strategies to approach this these problems.

(a)



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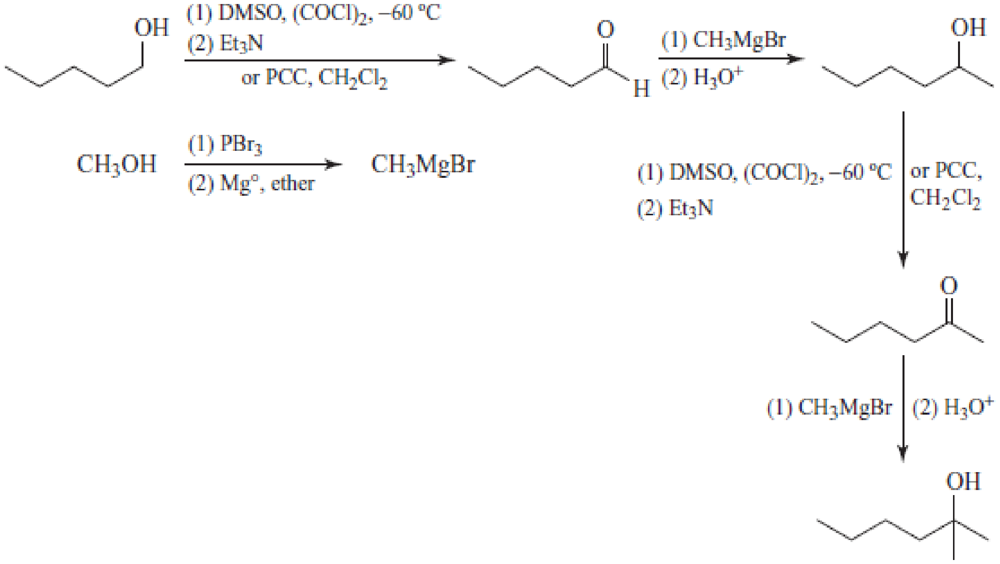

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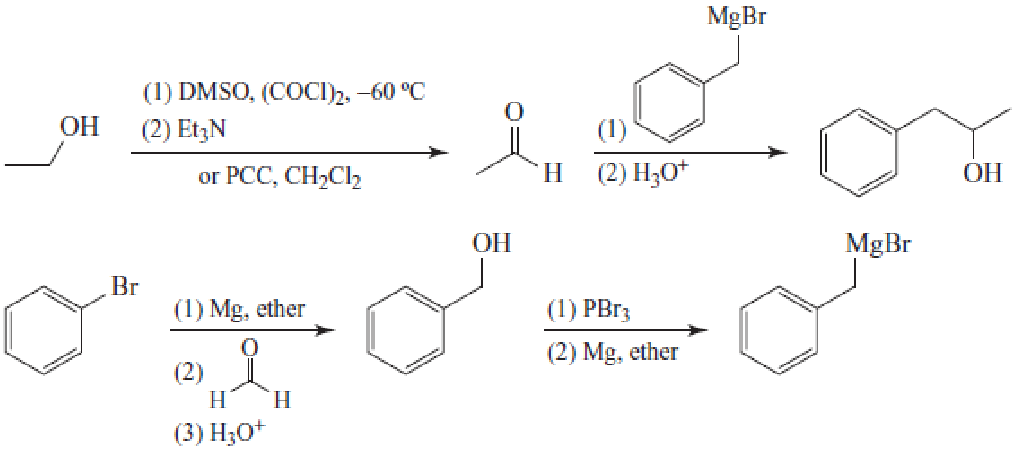

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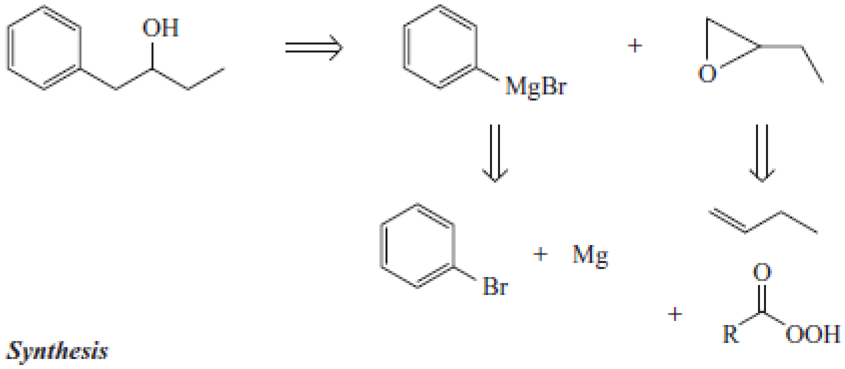
Retrosynthetic Analysis



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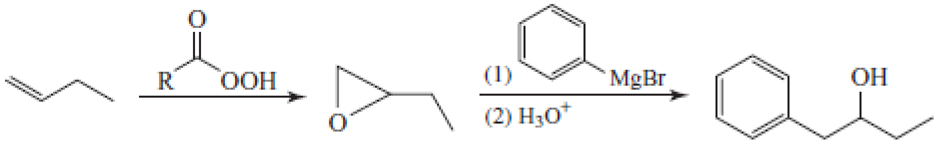

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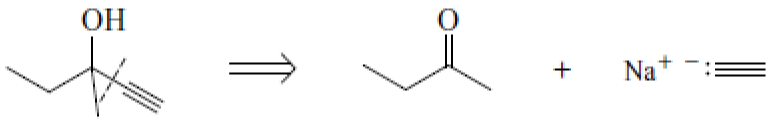
Retrosynthetic Analysis



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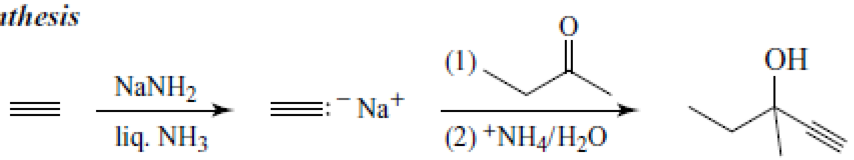

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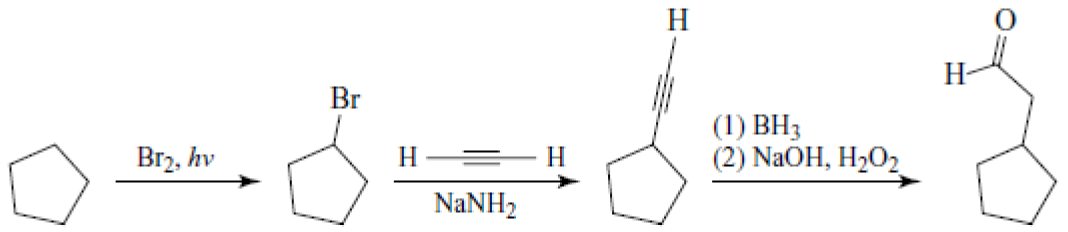

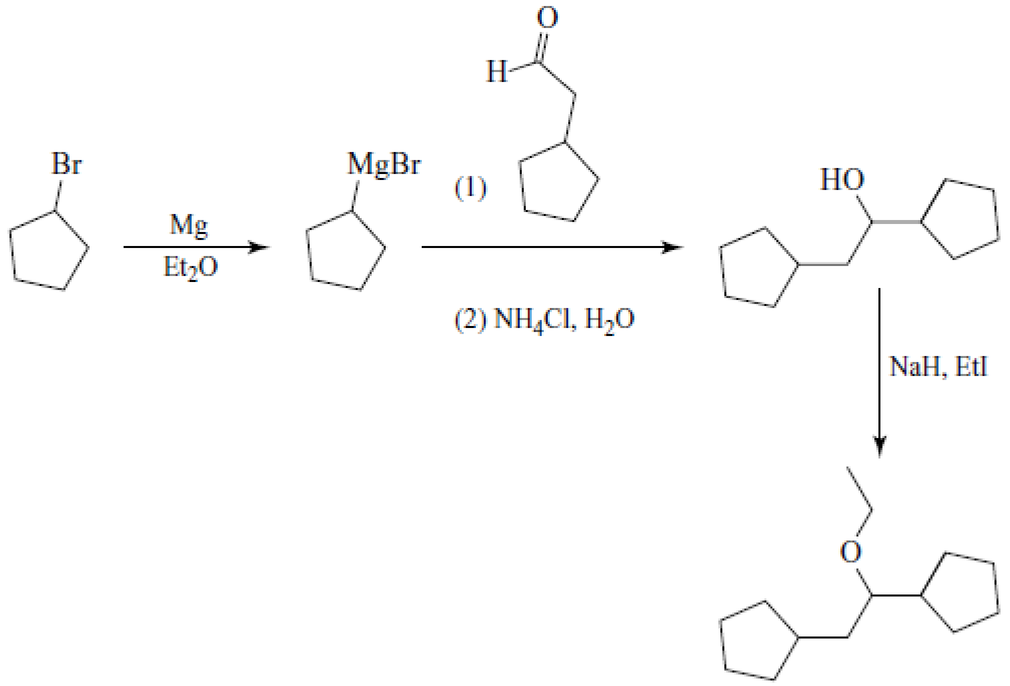

<H1> **ADDITIONAL OBJECTIVE QUESTIONS**

<H2> **Single Correct Choice Type**

1. **(d)** Secondary alcohol is oxidized to ketone.
2. **(d)** Both LAH and SBH (Sodium borohydride) are strong reducing agents.
3. **(a)** Nitro group is not reduced by SBH.
4.**(c)** More the electron deficiency of carbonyl carbon, more is the rate of reaction with Grignard reagent.
5. **(b)** Alkyne is not reduced by LAH.
6. **(a)** Grignard will give acid base reaction with alcohol by abstracting proton from it.
7. **(d)** The attacking hydride group comes from Sodium boro hydride.
8. **(b)** Grignard will give intramolecular acid base reaction and abstract proton from N, and then N^- will attack aldehyde.

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9. **(d)** First is oxidation while the second and third reactions are nucleophilic addition followed by oxidation.
10. **(a)** One mole each by aldehyde and alcohol, and two moles each by ester and acid halide.
11. **(b)** More the electron deficiency of carbonyl carbon, more is the rate of reaction with LAH.
12. **(b)** Alcohol isomers only would give the reaction.
13. **(b)** P will have OH substituted by Cl. In Q, N will substitute Cl to give amide, which is then reduced by LAH.

<H2> Multiple Correct Choice Type

1. **(b),(d)** The methyl group can add to the carbonyl group from same side or opposite side as the phenyl group, yielding geometrical isomers (diastereomers). The molecule has a plane of symmetry thus optically inactive.
2. **(b),(c),(d)** Grignard will yield tertiary alcohol with acid halide, ester and anhydride while it will give secondary alcohol with a as the H of acid halide will not be substituted.

<H2> Integer Type

1. **(4) and (2)** LAH will reduce all groups while SBH will not reduce ester and carboxylic acid.
2. **(2)** As per given reaction, only two equivalents are used by the ester group.
3. **(3)** Methyl will give addition at the carbonyl carbon. Products: both methyl groups on same side (meso) and methyl groups on opposite sides (two enantiomers).
4. **(3)** Tertiary alcohols would be formed at each ester. Products: both alcohol groups in cis (meso) and alcohol groups in trans (two enantiomers).

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<H2> Matrix Match Type

1. $a \rightarrow (p, r); b \rightarrow (r); c \rightarrow (s); d \rightarrow (p, r)$

Option (a) : Hydride addition will result in formation of alcohol and a chiral carbon.

Option (b) : Cyanide (nucleophile) will give addition reaction at the carbonyl carbon.

Option (c) : Cyanide (nucleophile) will give substitution with halide.

Option (d) : Grignard will give nucleophilic addition at the carbonyl carbon alongwith generation of chiral carbon.

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Chapter 12: Conjugated Unsaturated Systems

Practice Problems

12.1

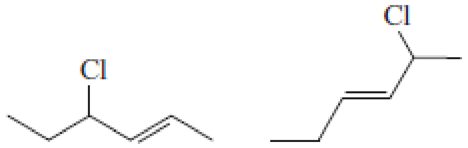
(a) (3*Z*)-Penta-1,3-diene, (2*E*,4*E*)-2,4-hexadiene, (2*Z*,4*E*)-hexa-2,4-diene, and 1,3-cyclohexadiene are conjugated dienes.

(b) 1,4-Cyclohexadiene and 1,4-pentadiene are isolated dienes.

(c) Pent-1-en-4-yne (1-penten-4-yne) is an isolated enyne.

12.2

(a)



+ stereoisomers   + stereoisomers

12.3

Addition of the proton gives the resonance hybrid.

(a)

I   **II**

The inductive effect of the methyl group in **I** stabilizes the positive charge on the adjacent carbon. Such stabilization of the positive charge does not occur in **II.** Because **I** contributes more heavily to the resonance hybrid than does **II,** C2 bears a greater positive charge and reacts faster with the bromide ion.

(b) In the 1,4-addition product, the double bond is more highly substituted than in the 1,2-addition product; hence it is the more stable alkene.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

Conjugated Systems

12.4

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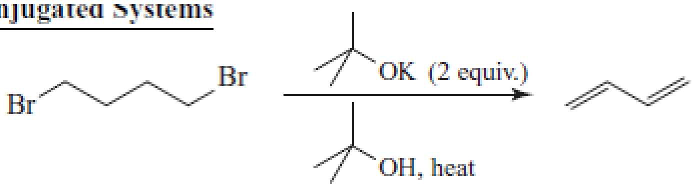
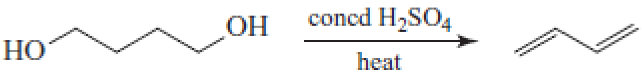
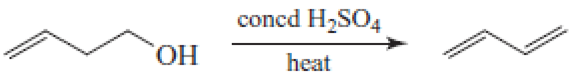
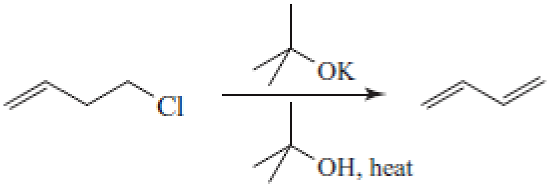
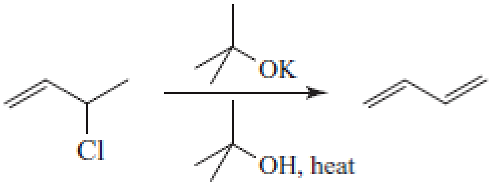
Conjugated Systems

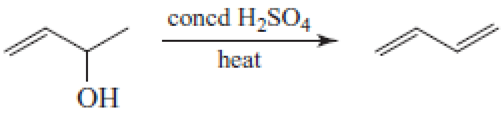
(a) 

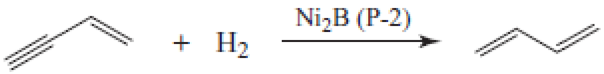
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

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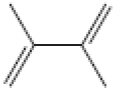
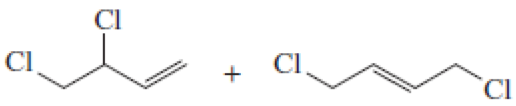
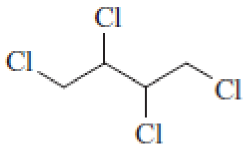


12.6

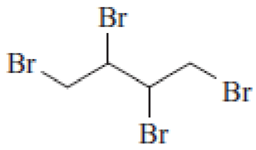
EY

(a) 

(racemic) + (*E*) + (*Z*)

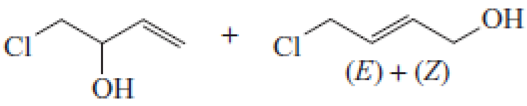
(b) 

(3 stereoisomers)

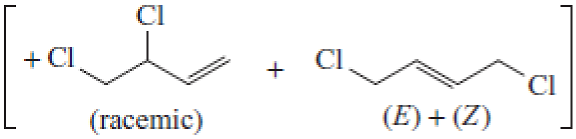
(c) 

(3 stereoisomers)

(d)

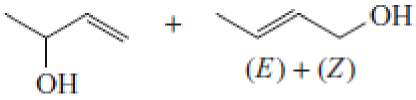
(e) 

(racemic) + (*E*) + (*Z*)



[+ (racemic) + (*E*) + (*Z*)]

(f) 4 CO_2 (*Note:* $KMnO_4$ oxidizes $HO_2C—CO_2H$ to 2 CO_2.)

(g) 

(racemic) + (*E*) + (*Z*)

12.7

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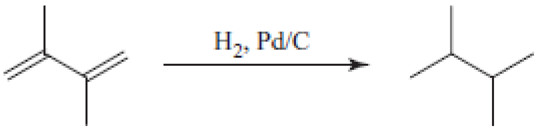
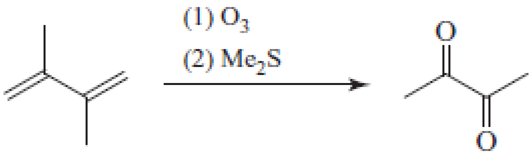
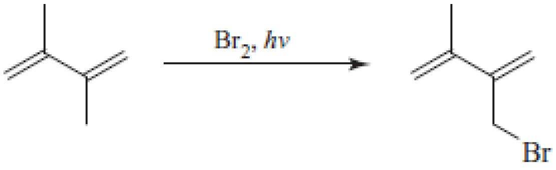
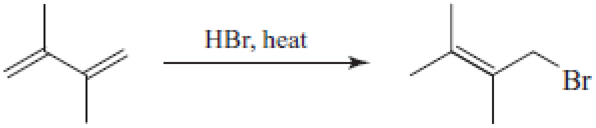
(a) 

(b) 

(c) 

(d) 

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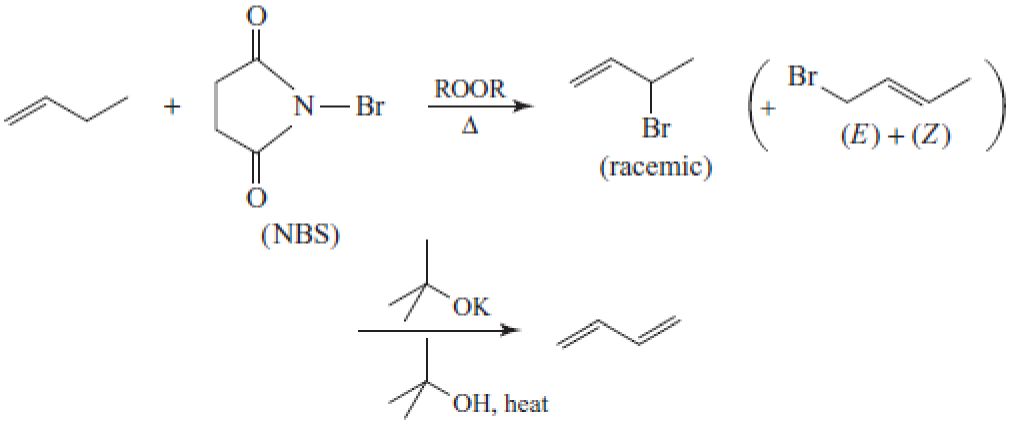
(a) 

Note: In the second step, both allylic halides undergo elimination of HBr to yield 1,3-butadiene; therefore, separating the mixture produced in the first step in unnecesary. The $BrCH_2CH{=}CHCH_3$ undergoes a 1,4-elimination (the opposite of a 1,4-addition).

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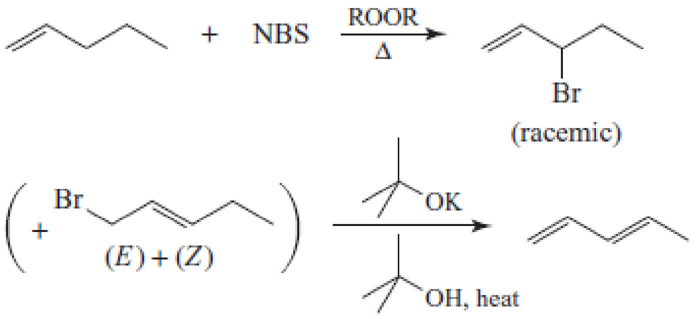
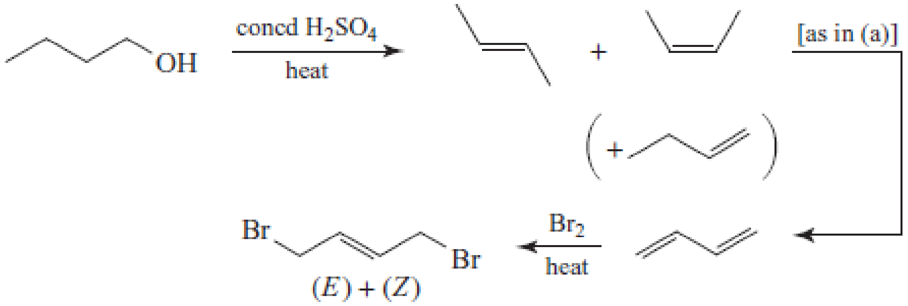
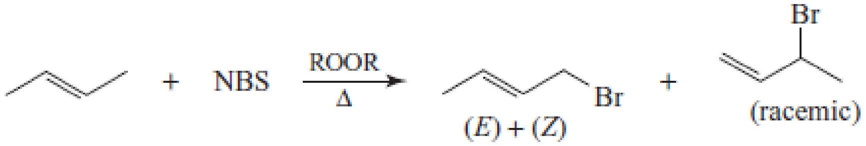
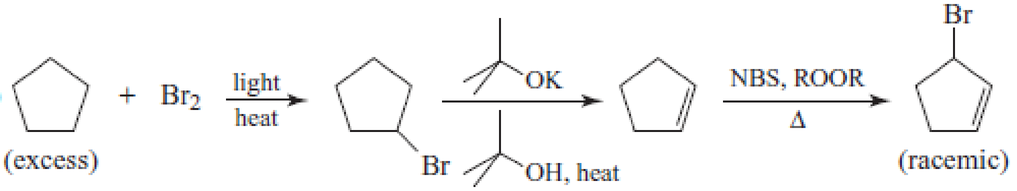
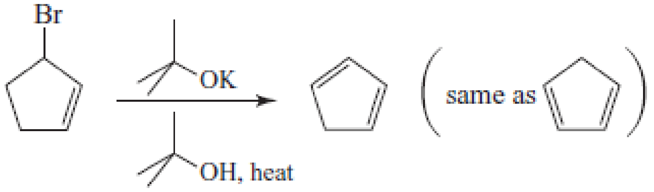
(b) 

Here again both products undergo elimination of HBr to yield 1,3-pentadiene.

(c) 

(d) 

(e) 

(f) 

12.9

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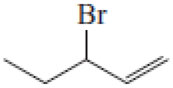
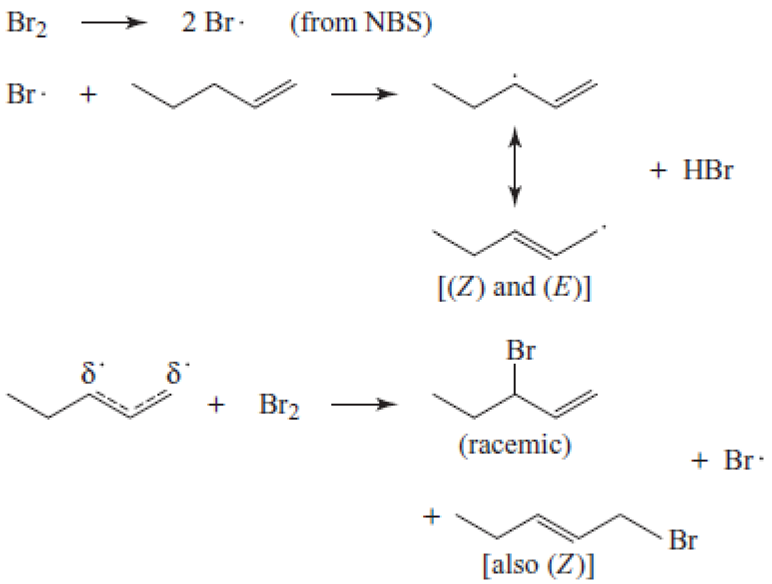
The products are  (racemic) and Br [also (*Z*)]. They are formed from an allylic radical in the following way:



12.10

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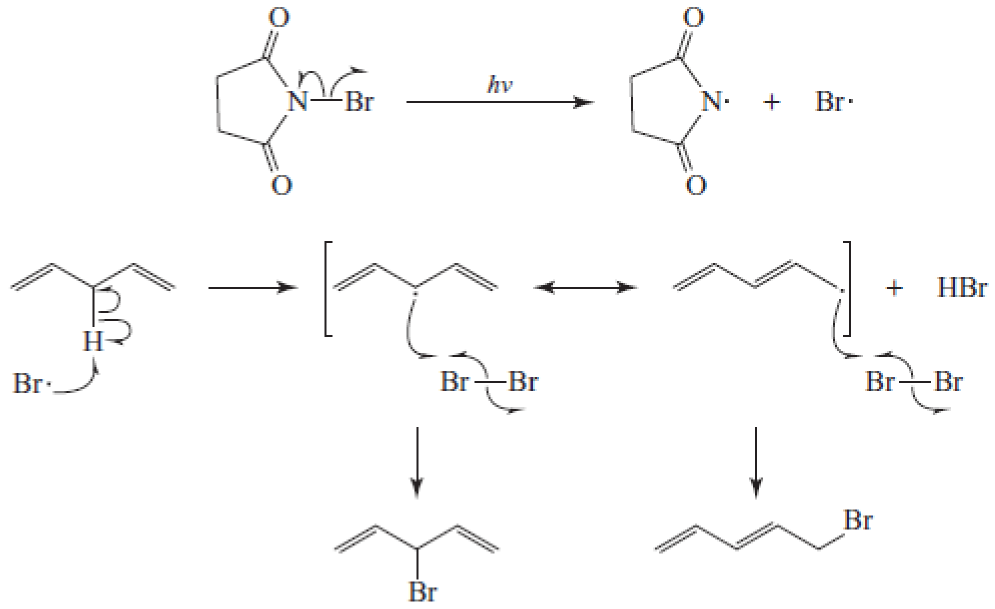
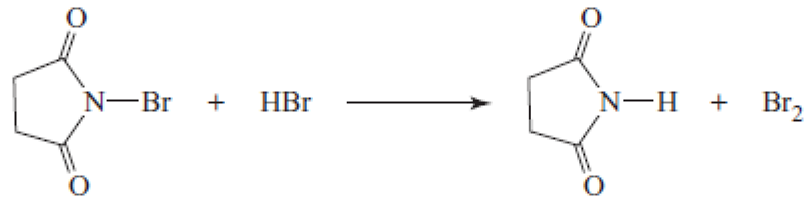


Where did the Br_2 come from? It was formed from NBS, as follows.



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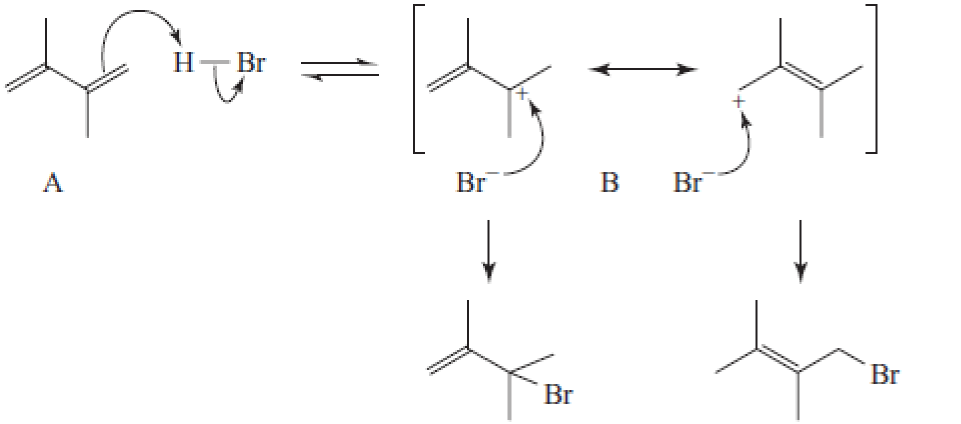

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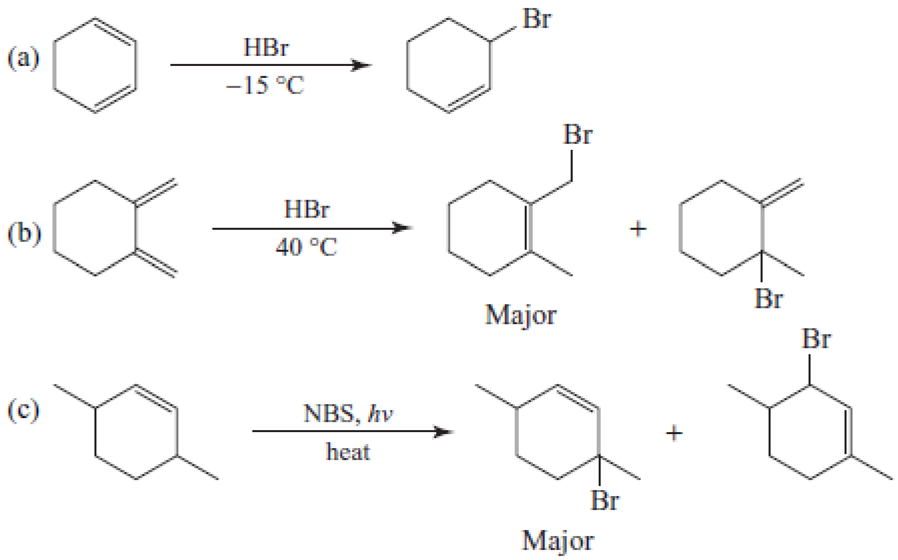
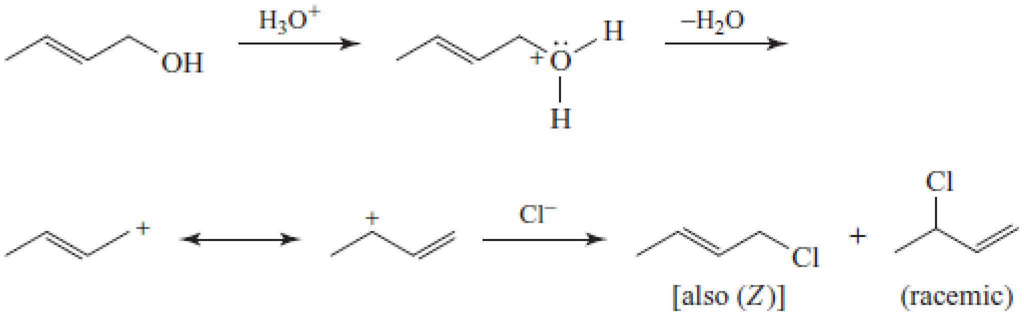
12.12



12.13

Protonation of the alcohol and loss of water leads to an allylic cation that can react with a chloride ion at either C1 or C3.



12.14

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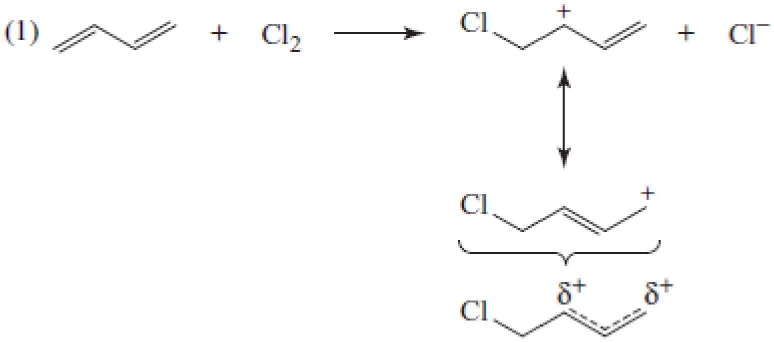
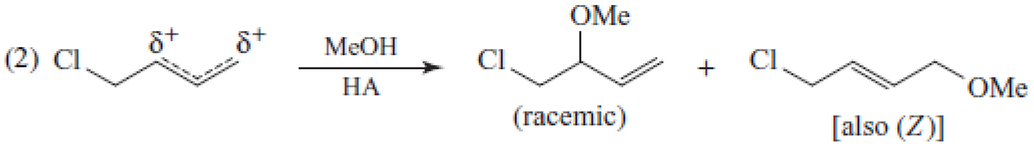
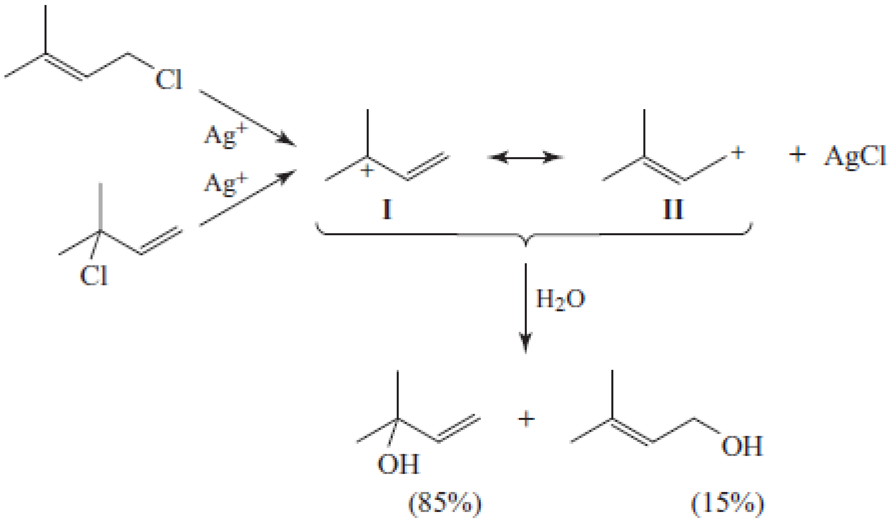




12.15

(a) The same carbocation (a resonance hybrid) is produced in the dissociation step:



(b) Structure **I** contributes more than **II** to the resonance hybrid of the carbocation (rule 8). Therefore, the hybrid carbocation has a larger partial positive charge on the tertiary carbon atom than on the primary carbon atom. Reaction of the carbocation with water will therefore occur more frequently at the tertiary carbon atom.

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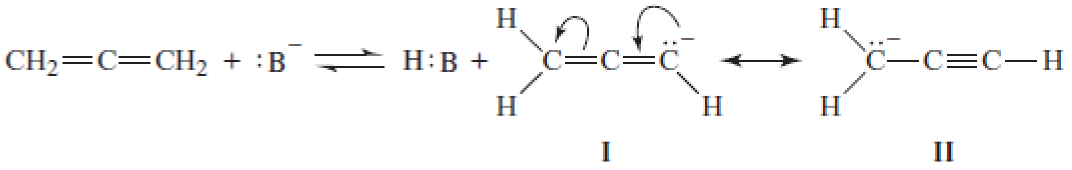
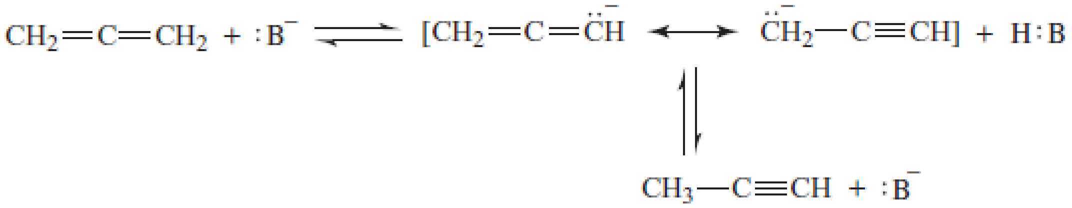
12.16

(a) Propyne. (b) Base (:B^-) removes a proton, leaving the anion whose resonance structures are shown:



Reaction with H:B may then occur at the CH_2 carbanion (**II**). The overall reaction is



12.17

The product formed when 1-bromobutane undergoes elimination is 1-butene, a simple monosubstituted alkene. When 4-bromo-1-butene undergoes elimination, the product is 1,3-butadiene, a conjugated diene, and therefore, a more stable product. The transition states leading to the products reflect the relative stabilities of the products. Since the transition state leading to 1,3-butadiene has the lower free energy of activation of the two, the elimination reaction of 4-bromo-1-butene will occur more rapidly.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

2. **(a)** Carbocation intermediate is formed which can undergo rearrangement.

3. (a) NBS gives substitution of α H forming most stable free radical with Br.
4. **(d)** The carbocation formed on addition of Bromonium to alkene would be attacked by lone pair of N.
5. **(a)** NBS gives substitution of α H forming most stable free radical with Br.

6. **(d)** Cl is substituted by OH and then hydroxide is removed to give carbocation which then undergoes cyclisation.
7. **(b)** NBS will substitute α H of alkene with Br which will then form Grignard reagent. Grignard will attack carbonyl C atom and then the oxide will give substitution with ethyl bromide. The C-C π bond of B is then oxidized to form C.
8. **(c)** The alkyl anion would give addition with alkene to again form carbanion which will give nucleophilic substitution with alkyl halide.

9. **(d)** All are possible from the free radical intermediate as it can also undergo resonance.

<H2> Multiple Correct Choice Type

1. (a),(b) Carbocation intermediate will undergo resonance.
2. **(a),(c),(d)** NBS gives substitution of α H.
3. **(a),(b)** Carbocation will be formed at the allylic position of either of the two pi bonds and may also undergo resonance. The carbocation is then attacked by Cl^- ion.
4. **(a),(b),(d)** In first step, bromonium (Br^+) will be added and then the carbocation formed will be attacked by nucleophile bromide (Br^-) ion.

<H2> Matrix Match Type

1. $a \rightarrow (q); b \rightarrow (p); c \rightarrow (s); d \rightarrow (r)$

Option (a): NBS gives substitution of α H.

Option (b): Cl will be substituted at α H by SO_2Cl_2/hv.

Option (c): SO_2Cl_2/hv will substitute Cl at the higher degree C and then NBS gives substitution of Br at the other C.

Option (d): NBS will substitute Br at the higher degree C and then SO_2Cl_2/hv gives substitution of Cl at the other C.

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Chapter 13: Aromatic Compounds

Practice Problems

13.1

(a) 4-Bromobenzoic acid (or *p*-bromobenzoic acid)

(b) 2-Benzyl-1.3-cyclohexadiene

(c) 2-Chloro-2-phenylpentane

(d) Phenyl propyl ether

13.2

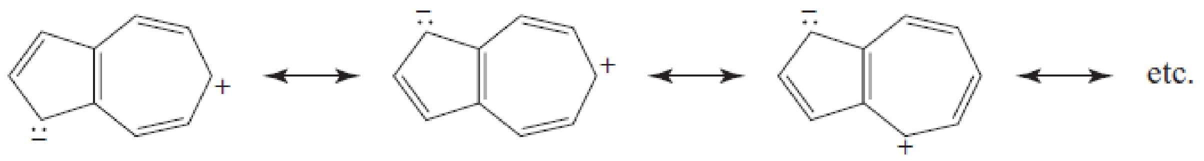
Compounds (a) and (b) would yield only one monosubstitution product.

13.3

Resonance structures are defined as being structures that differ *only* in the positions of the electrons. In the two 1,3,5-cyclohexatrienes shown, the carbon atoms are in different positions; therefore, they cannot be resonance structures.

13.4

Major contributors to the hybrid must be ones that involve separated charges. Contributors like the following would have separated charges, and would have aromatic five- and seven-membered rings.



Review Problems

Nomenclature

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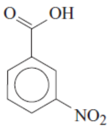
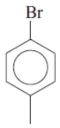
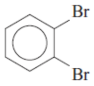
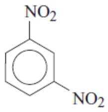
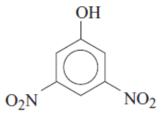
13.5

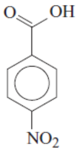
(a) 

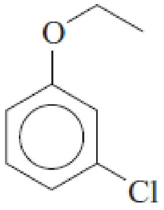
(b) 

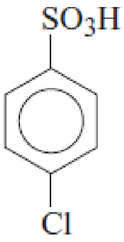
(c) 

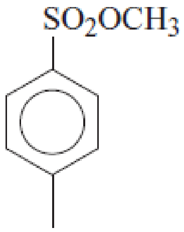
(d) 

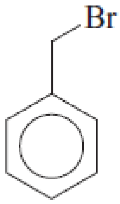
(e) 

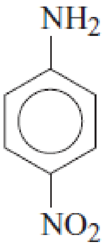
(f) 

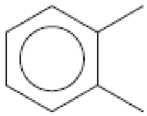
(g) 

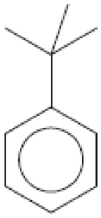
(h) 

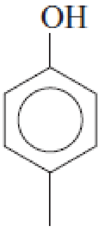
(i) 

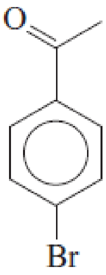
(j) 

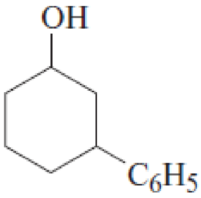
(k) 

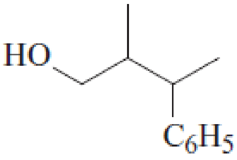
(l) 

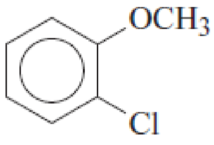
(m) 

(n) 

(o) 

(p) 

(q) 

(r) 

13.6

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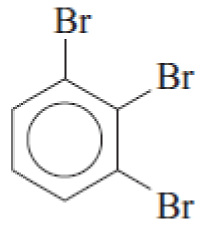
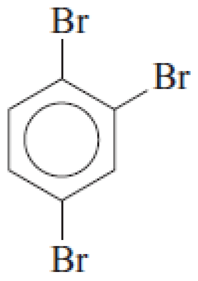
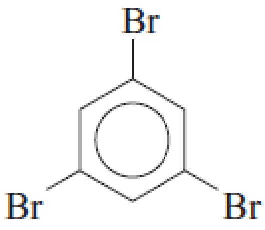


1,2,3-Tribromo-
benzene



1,2,4-Tribromo-
benzene



1,3,5-Tribromo-
benzene

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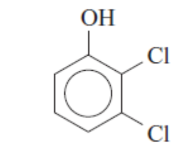
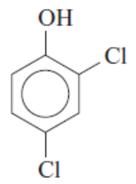
(b)



2,3-Dichloro-
phenol



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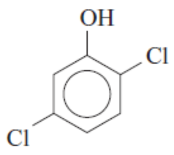
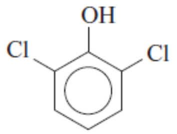
phenol



2,5-Dichloro-
phenol



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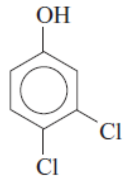
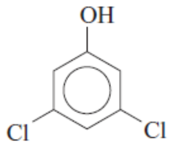
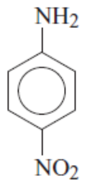


3,4-Dichloro-
phenol

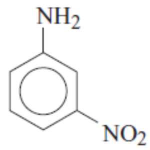


3,5-Dichloro-
phenol

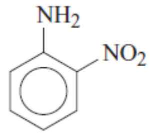
(c)



4-Nitroaniline
(*p*-nitroaniline)

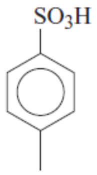


3-Nitroaniline
(*m*-nitroaniline)

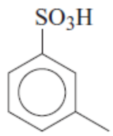


2-Nitroaniline
(*o*-nitroaniline)

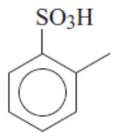
(d)



4-Methylbenzene-
sulfonic acid
(*p*-toluenesulfonic
acid)

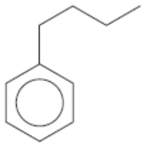


3-Methylbenzene-
sulfonic acid
(*m*-toluenesulfonic
acid)

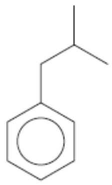


2-Methylbenzene-
sulfonic acid
(*o*-toluenesulfonic
acid)

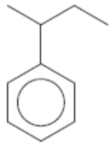
(e)



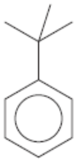
Butylbenzene



Isobutylbenzene



sec-Butylbenzene



tert-Butylbenzene

Aromaticity

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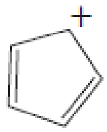
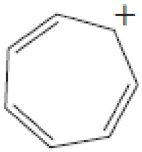
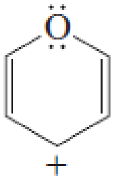
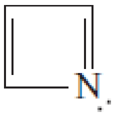
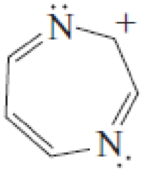
13.7

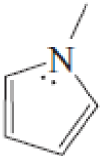
(a)  Antiaromatic

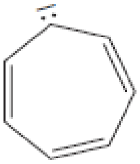
(b)  Aromatic

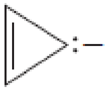
(c)  Aromatic

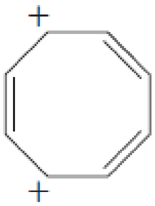
(d)  Antiaromatic

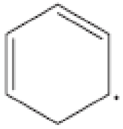
(e)  Aromatic

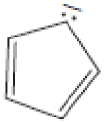
(f)  Aromatic

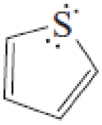
(g)  Antiaromatic

(h)  Antiaromatic

(i)  Aromatic

(j)  Nonaromatic

(k)  Aromatic

(l)  Aromatic

13.8

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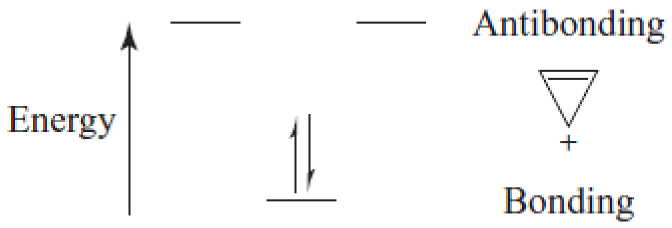
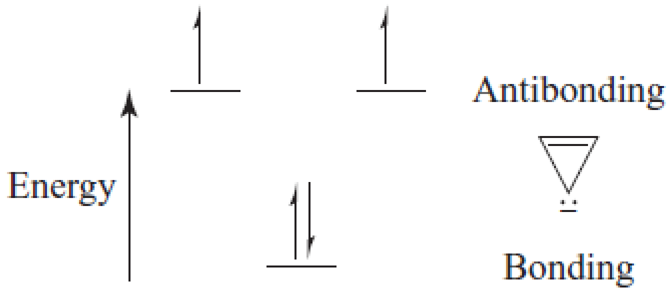
(a) 

(b) 

13.9

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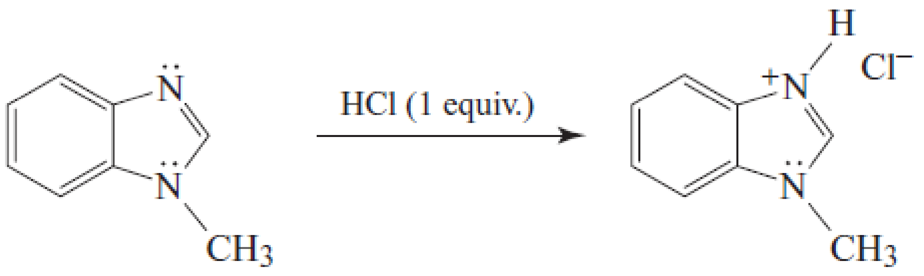
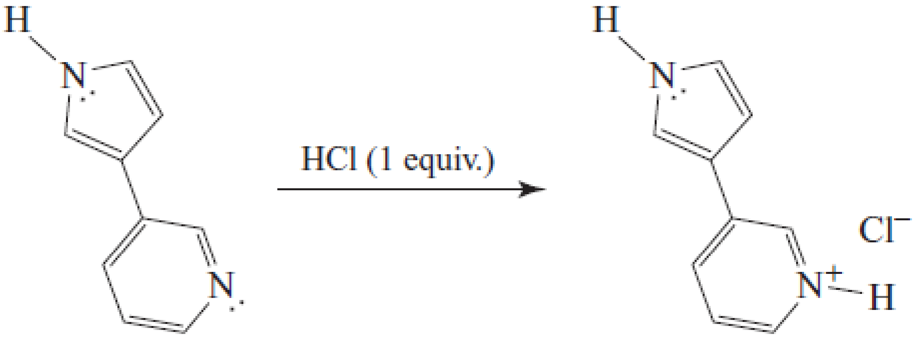
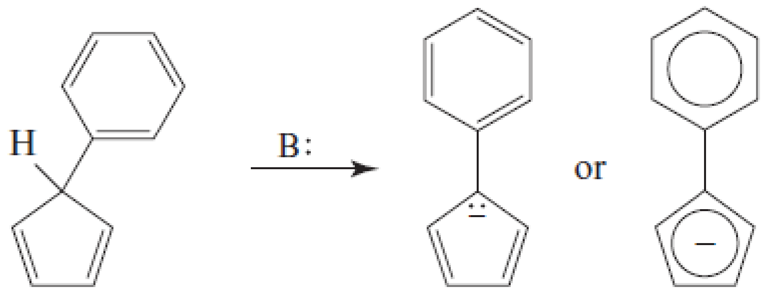
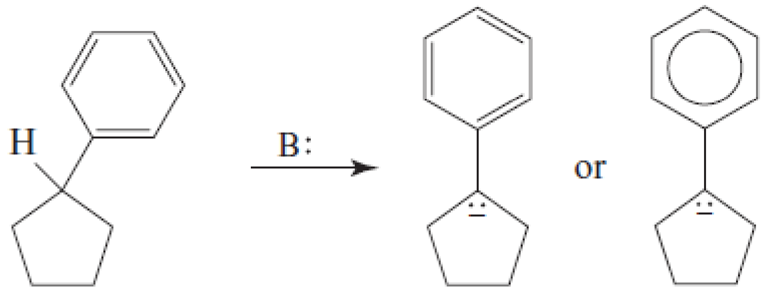
(a) 

(b) 

13.10



A



B

The conjugate base of **A** is a substituted cyclopentadienyl anion and both rings are aromatic. In **B**, the five-membered ring does not contribute to anion stability. The additional stabilization provided by the cyclopentyldienyl moiety is the reason for the greater acidity of **A**.

13.11

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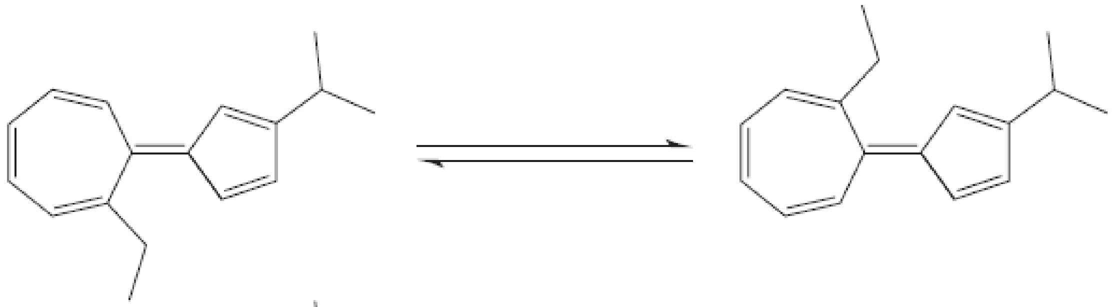
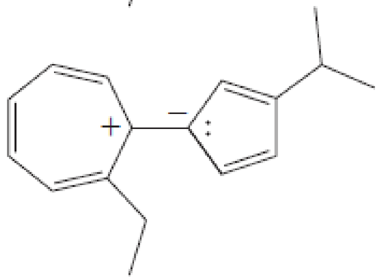




The major resonance form leaves the electrons in the cyclopentadiene ring to make both rings aromatic. Therefore, the central bond has more single bond character and rotation around that bond is easily achieved.

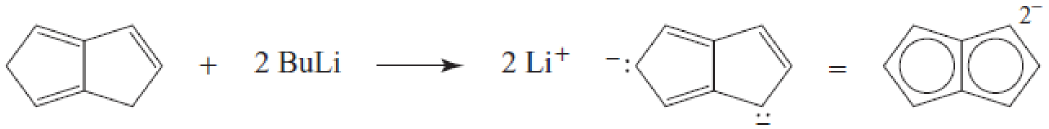
13.12

Hückel's rule should apply to both pentalene and heptalene. Pentalene's antiaromaticity can be attributed to its having 8 π electrons. Heptalene's lack of aromaticity can be attributed to its having 12 π electrons. Neither 8 nor 12 is a Hückel number.

13.13

(a) The extra two electrons go into the two partly filled (nonbonding) molecular orbitals (Fig. 14.7), causing them to become filled. The dianion, therefore, is not a diradical. Moreover, the cyclooctatetraene dianion has 10 π electrons (a Hückel number), and this apparently gives it the stability of an aromatic compound. (The highest occupied molecular orbitals may become slightly lower in energy and become bonding molecular orbitals.) The stability gained by becoming aromatic is apparently large enough to overcome the extra strain involved in having the ring of the dianion become planar.

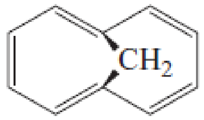
(b) The strong base (butyllithium) removes two protons from the compound on the left. This acid-base reaction leads to the formation of the 10 π electron pentalene dianion, an aromatic dianion.



Pentalene dianion

13.14

The bridging —CH_2— group causes the 10 π electron ring system (below) to become planar. This allows the ring to become aromatic.



13.15

Ionization of 5-chloro-1,3-cyclopentadiene would produce a cyclopentadienyl cation, and the cyclopentadienyl cation (see Problem 14.8) would be highly unstable because it would be antiaromatic.

Antiaromatic ion
(highly unstable)

13.16

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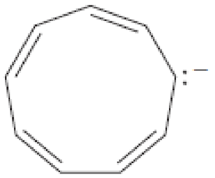
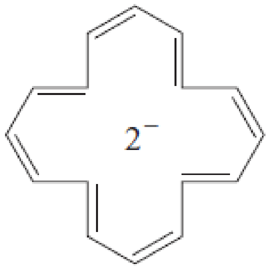
(a) The cyclononatetraenyl anion with 10 π electrons obeys Hückel's rule.



Cyclononatetraenyl anion
10 π electrons
Aromatic



Cyclohexadecaoctaenyl dianion
18 π electrons
Aromatic

(b) By adding 2 π electrons, [16] annulene becomes an 18 π electron system and therefore obeys Hückel's rule.

13.17

As noted in Problem 13.42, furan can serve as the diene component of Diels-Alder reactions, readily losing all aromatic character in the process. Benzene, on the other hand, is so unreactive in a Diels-Alder reaction that it can be used as a nonreactive solvent for Diels-Alder reactions.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (b) It is planar so that it can be aromatic.

2. **(d)** It follows Huckel's rule ($4n+2\pi\ e^-$).

3. **(a)** Cyclooctatetraene does not have resonance as it is non-planar and has tub shape. Hence ii has pure double bond character and iii has pure single bond character. IV is pure triple bond character thus it is the shortest of the four while i is somewhere between a double and a single bond due to resonance.

4.**(d)** It is anti-aromatic.

5. **(b)** It will readily lose to proton as the conjugate base is aromatic and thus highly stabilised.

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6. (c) First is aromatic while the second is non-aromatic.

7. **(d)** It has incomplete delocalisation.

8. **(b)** To avoid being anti-aromatic as it would then be destabilized.

9. **(b)** C1-C2 bond is shorter as it has more double bond character (double bond in 2 out of three resonating structures) as compared to C2-C3 bond (one out of three resonating structures)

10. **(c)** A will be reduced as it would result in the elimination of three anti-aromatic rings.

<H2> Linked Comprehension Type

1. **(c)** It is aromatic.

2. **(d)** It is non planar.

3. **(b)** More the stability of carbocation formed upon removal of iodide, more it the rate of reaction with $AgNO_3$.

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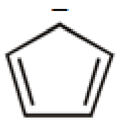
<H2> Integer Type

1. **(6)** It is cyclopentadienyl anion.



<H2> Matrix Match Type

1. $a \rightarrow (p, s, w); b \rightarrow (p, s, w); c \rightarrow (q, x, y, z); d \rightarrow (q, w, y)$

Option (a): It is aromatic, planar and follows Huckel's rule.

Option (b): It is aromatic, planar and follows Huckel's rule.

Option (c): It is non-planar thus non-aromatic. It reacts with active metals to gain two e^- and thus turn aromatic.

Option (d): It is non-planar thus non-aromatic.

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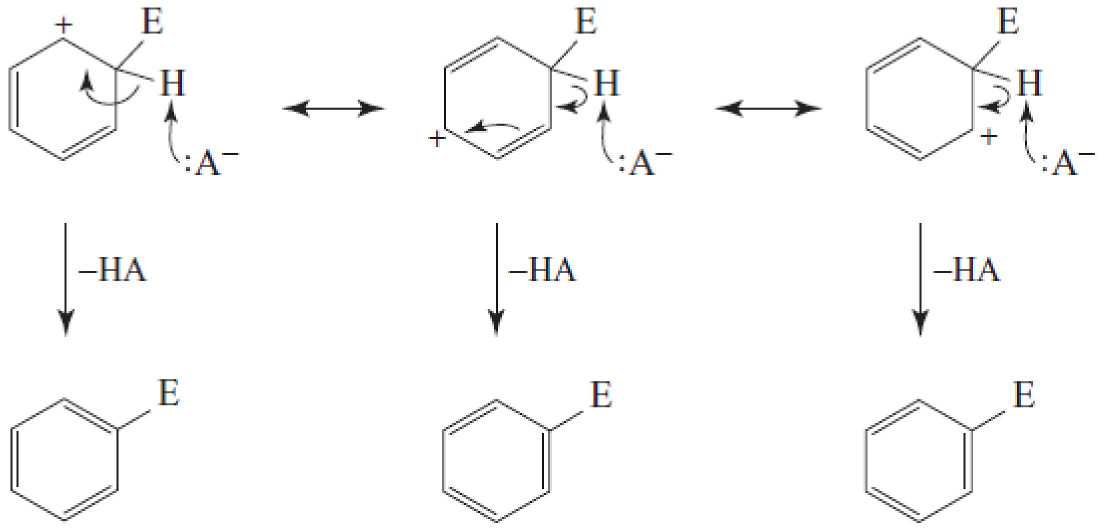
Chapter 14: Reactions of Aromatic Compounds

Practice Problems

14.1



14.2

WILEY

The rate is dependent on the concentration of NO_2^+ ion formed from protonated nitric acid.

$$H-\overset{+}{O}(H)-NO_2 \quad + \quad HA \longrightarrow NO_2^+ \quad + \quad H_3O^+ \quad + \quad A^-$$

(where HA = HNO_3 or $HOSO_3H$)

Because H_2SO_4 ($HOSO_3H$) is a stronger acid, a mixture of it and HNO_3 will contain a higher concentration of protonated nitric acid than will nitric acid alone.

That is, the reaction,

$$H-O-NO_2 \quad + \quad HOSO_3H \rightleftharpoons H-\overset{+}{O}(H)-NO_2 \quad + \quad HSO_4^-$$

Protonated nitric acid

produces more protonated nitric acid than the reaction,

$$H-O-NO_2 \quad + \quad H-O-NO_2 \rightleftharpoons H-\overset{+}{O}(H)-NO_2 \quad + \quad NO_3^-$$

14.3

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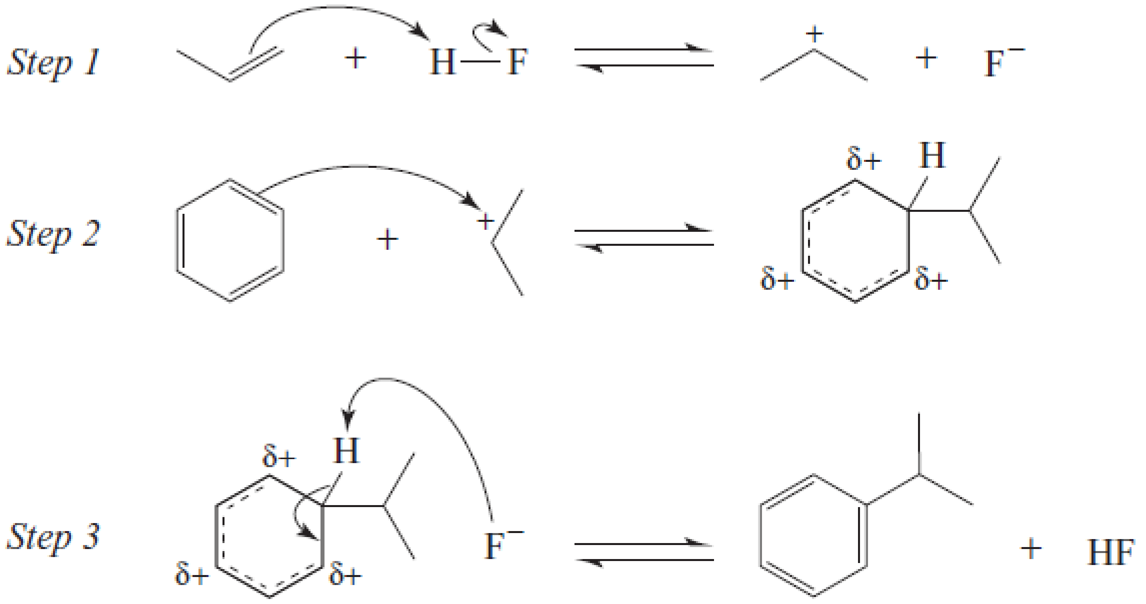
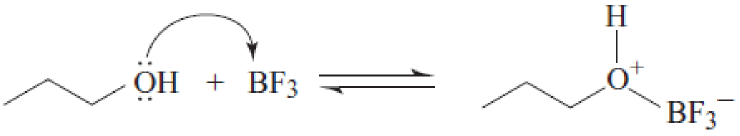
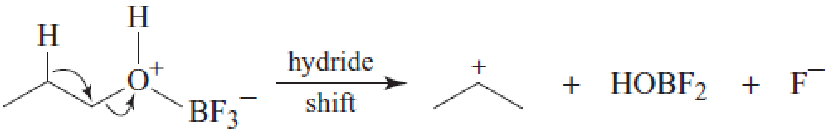


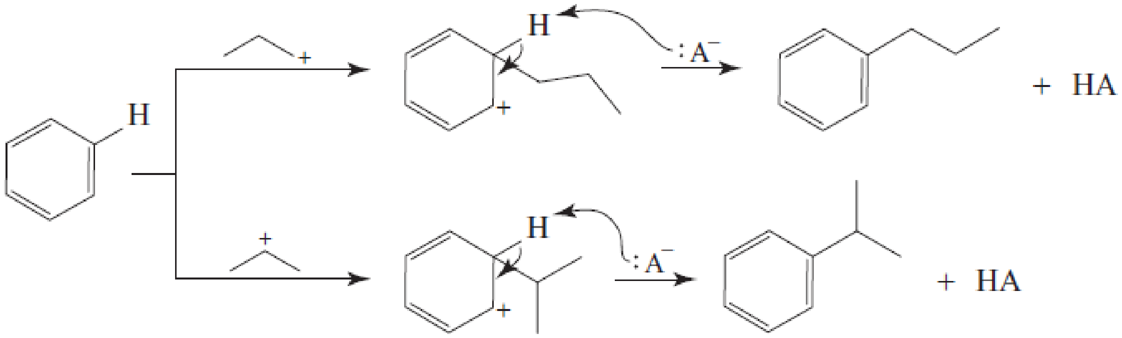
14.4



Rearrangement to the secondary carbocation occurs as the leaving group departs.



Both carbocations are then attacked by the ring.



14.5

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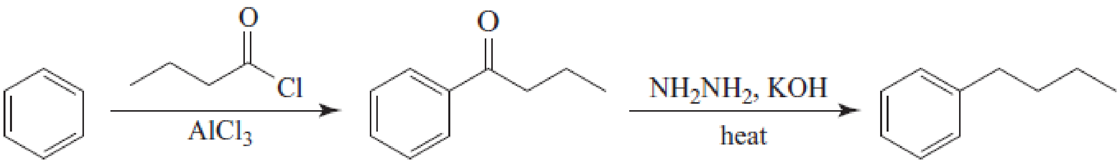
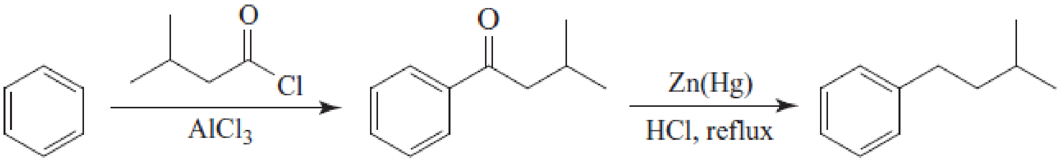
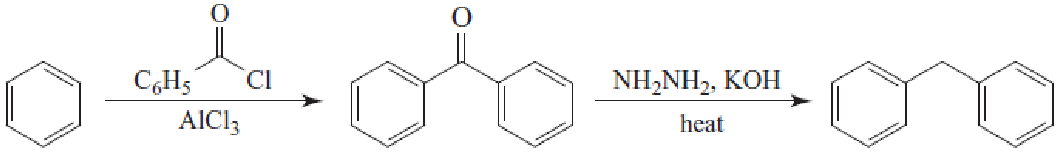
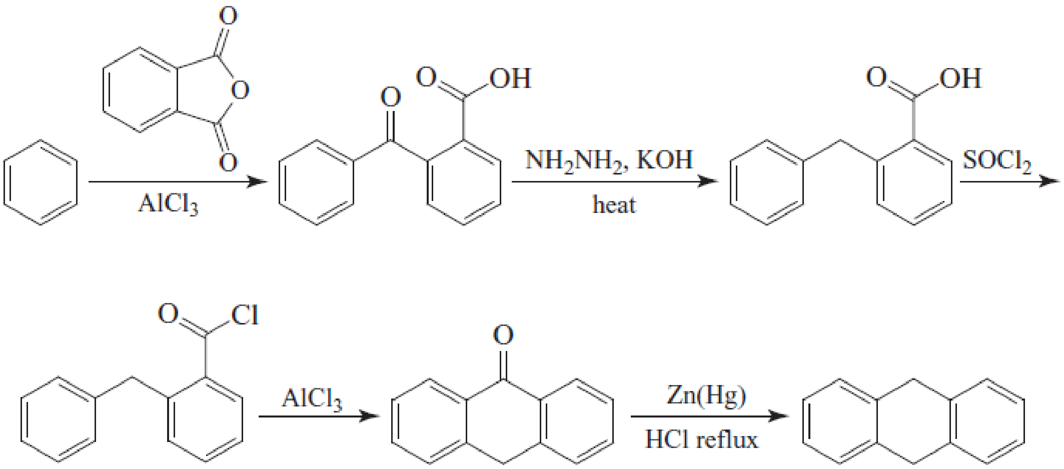
(a) 

(b) 

(c) 

(d) 

14.6

If the methyl group had no directive effect on the incoming electrophile, we would expect to obtain the products in purely statistical amounts. Since there are two ortho hydrogen atoms, two meta hydrogen atoms, and one para hydrogen, we would expect to get 40% ortho (2/5), 40% meta (2/5), and 20% para (1/5). Thus, we would expect that only 60% of the mixture of mononitrotoluenes would have the nitro group in the ortho or para position. And we would expect to obtain 40% of *m*-nitrotoluene. In actuality, we get 96% of combined *o*- and *p*-nitrotoluenes and only 4% *m*-nitrotoluene. This shows the ortho-para directive effect of the methyl group.

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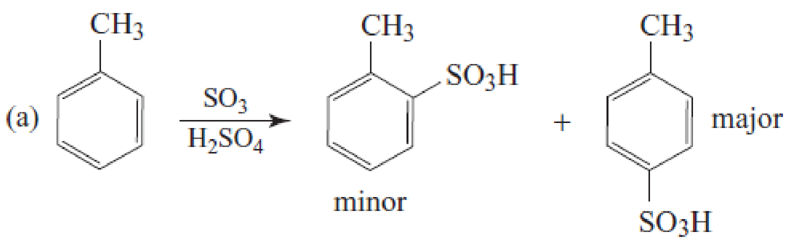
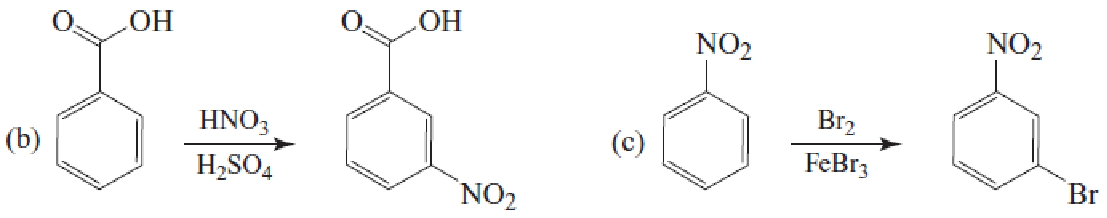
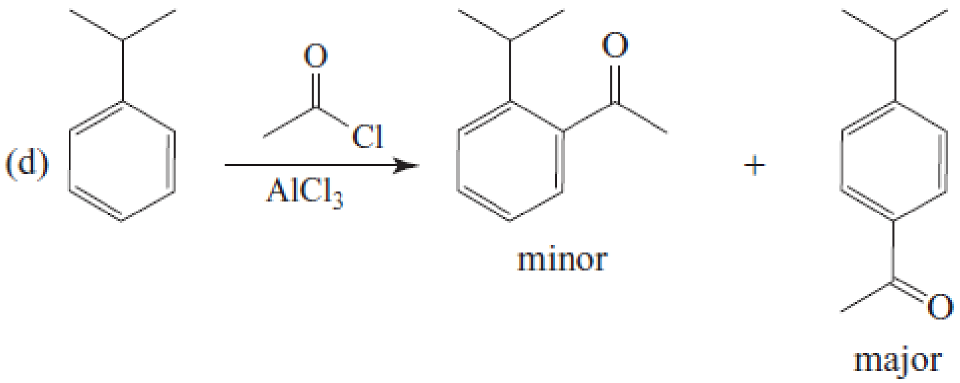
14.7







14.8

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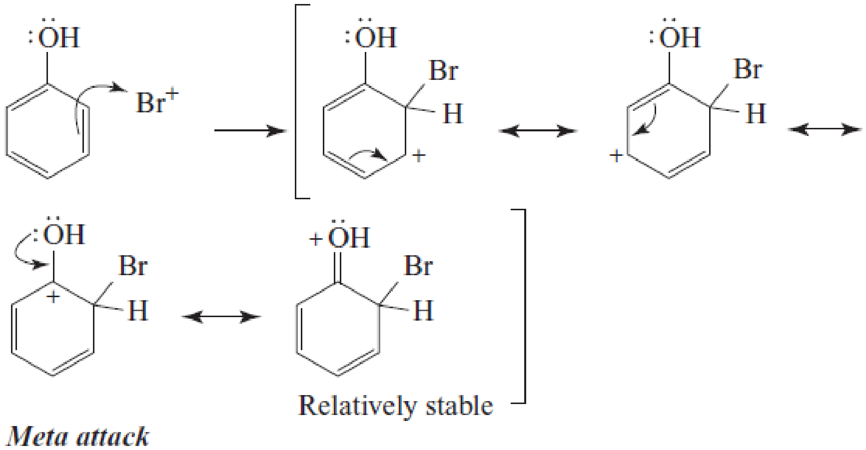
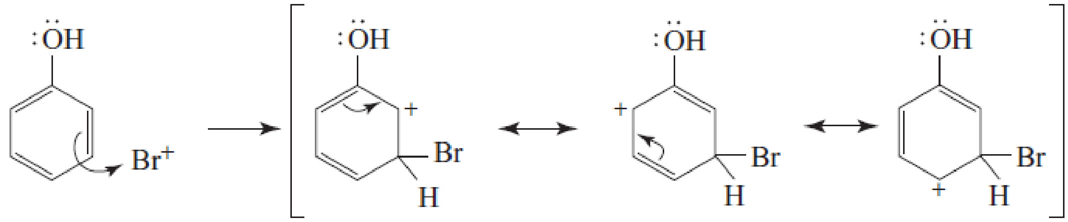
As the following structures show, attack at the ortho and para positions of phenol leads to arenium ions that are more stable (than the one resulting from meta attack) because they are hybrids of four resonance structures, one of which is relatively stable. Only three resonance structures are possible for the meta arenium ion, and none is relatively stable.

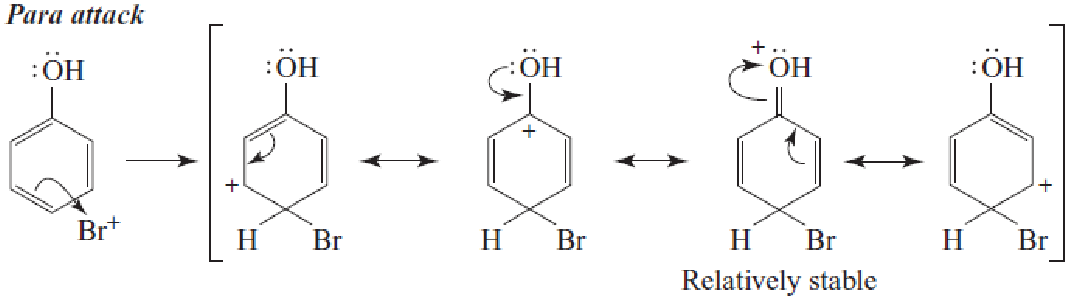
Ortho attack



Meta attack



Para attack



14.9

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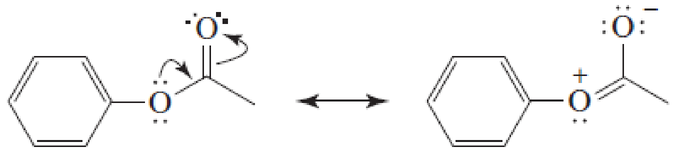
(a) The atom (an oxygen atom) attached to the benzene ring has an unshared electron pair that it can donate to the arenium ions formed from ortho and para attack, stabilizing them. (The arenium ions are analogous to the previous answer with a —$COCH_3$ group replacing the —H of the phenolic hydroxyl).

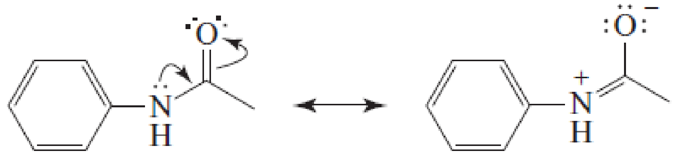
(b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.



This effect makes the benzene ring of phenyl acetate less electron rich and, therefore, less reactive.

(c) Because the acetamido group has an unshared electron pair on the nitrogen atom that it can donate to the benzene ring, it is an ortho-para director.

(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.



14.10

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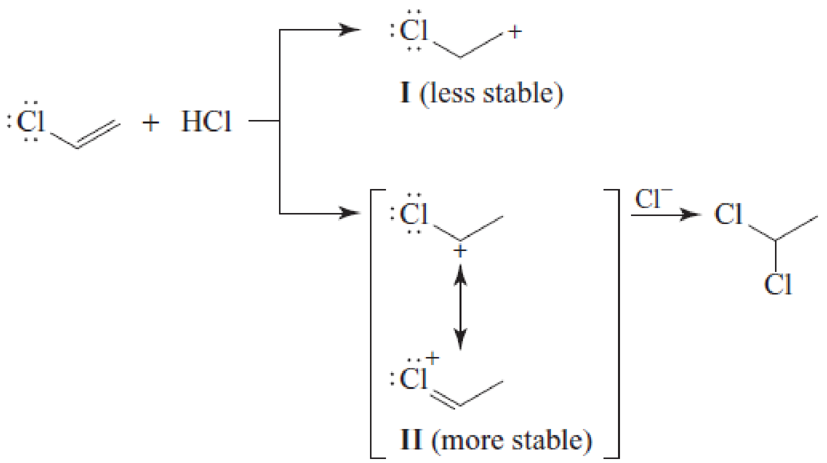
The electron-withdrawing inductive effect of the chlorine of chloroethene makes its double bond less electron rich than that of ethene. This causes the rate of reaction of chloroethene with an electrophile (i.e., a proton) to be slower than the corresponding reaction of ethene.

When chloroethene adds a proton, the orientation is governed by a resonance effect. In theory, two carbocations can form:



Carbocation **II** is more stable than **I** because of the resonance contribution of the extra structure just shown in which the chlorine atom donates an electron pair (see Section 15.11D).

14.11

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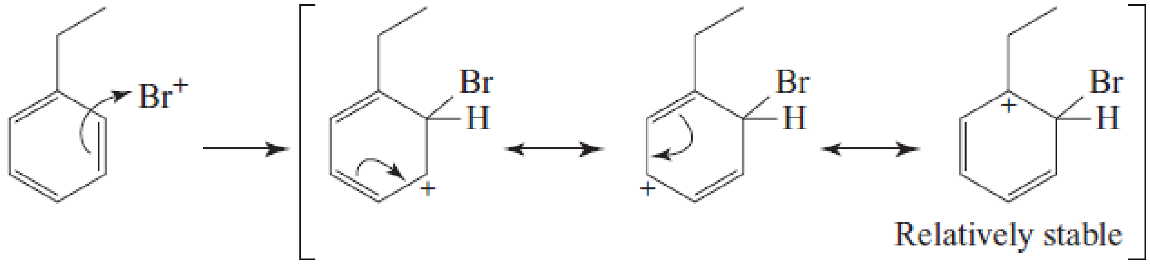
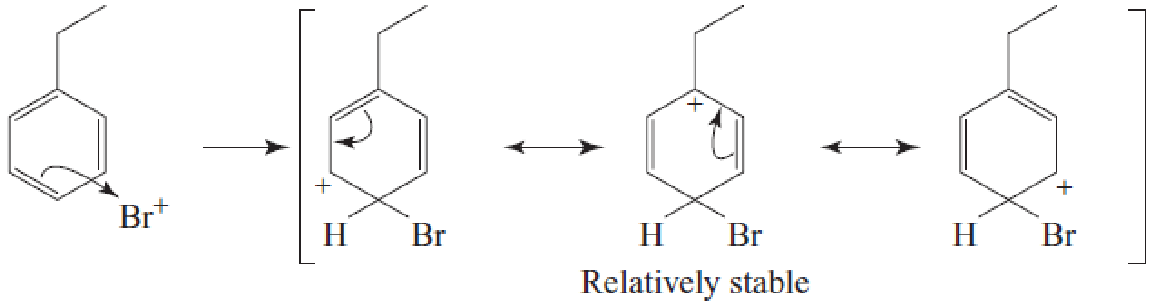
Ortho attack



Para attack



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14.12

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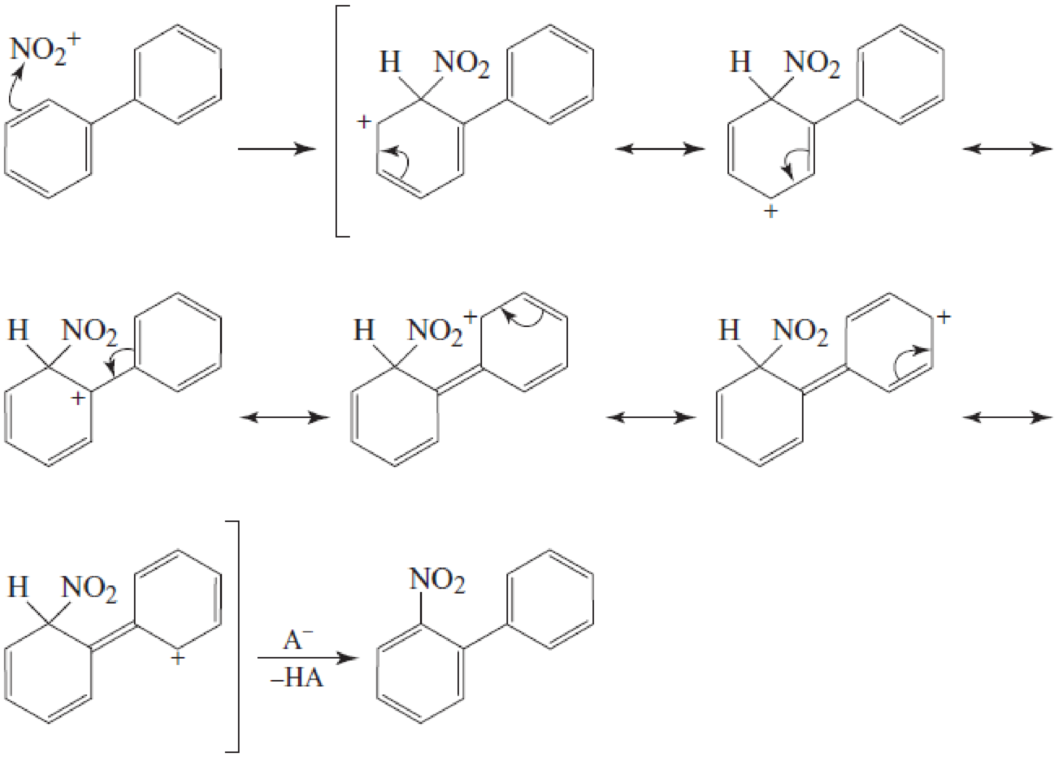
The phenyl group, as the following resonance structures show, can act as an electron-releasing group and can stabilize the arenium ions formed from ortho and para attack.

Ortho attack



In the case of the arenium ions above and following, the unsubstituted ring can also be shown in the alternative Kekule structure.

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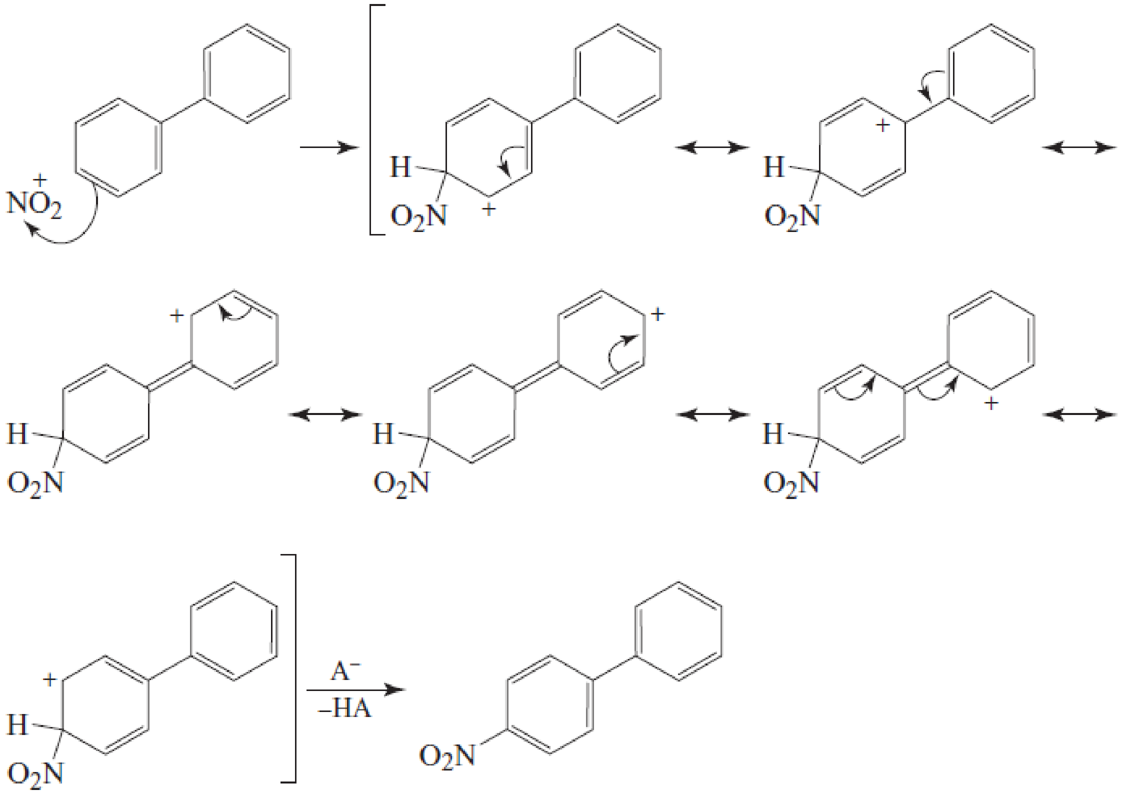
Para attack



In the case of both ortho and para substitution, the phenyl group functions as an activating group, resulting in a faster reaction then in the case of benzene.

14.13

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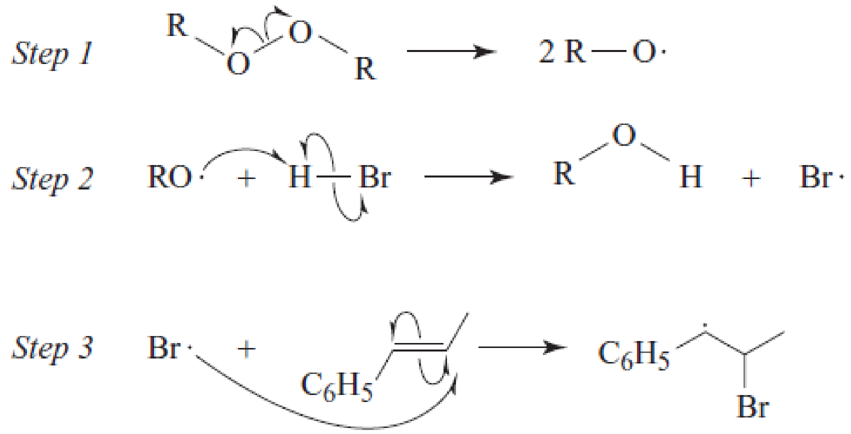
The addition of hydrogen bromide to 1-phenylpropene proceeds through a benzylic radical in the presence of peroxides, and through a benzylic cation in their absence (cf., a and b as follows).

(a) Hydrogen bromide addition in the presence of peroxides.

Chain Initiation



A benzylic radical

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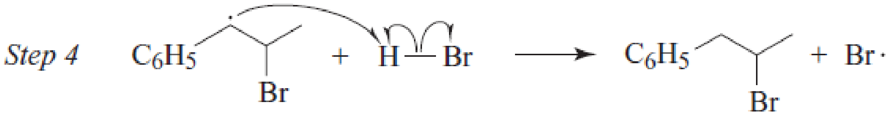
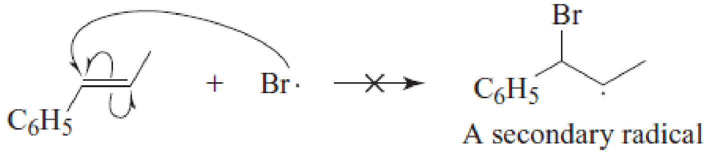
Chain Propagation



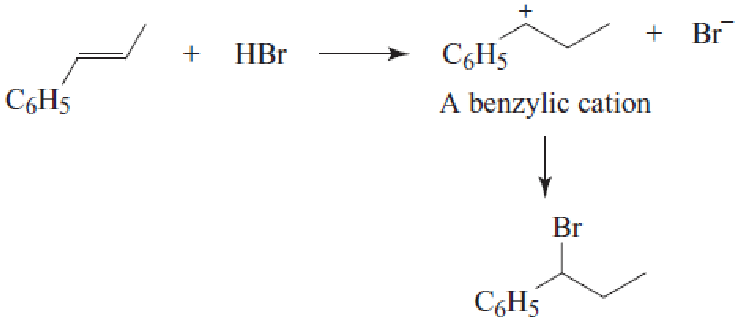
2-Bromo-1-phenylpropane

The mechanism for the addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.



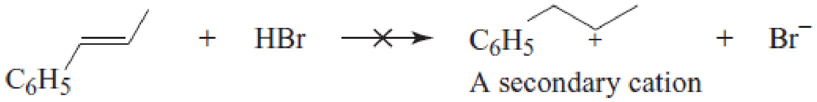
A secondary radical

(b) Hydrogen bromide addition in the absence of peroxides.



1-Bromo-1-phenylpropane

In the absence of peroxides, hydrogen bromide adds through an ionic mechanism. The step that determines the orientation in the ionic mechanism is the first, where the proton attacks the double bond to give the more stable benzylic cation. Had the proton attacked the double bond in the opposite way, a less stable secondary cation would have been formed.



A secondary cation

14.14

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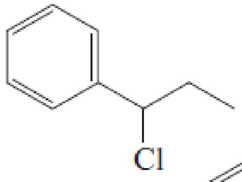
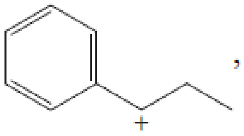
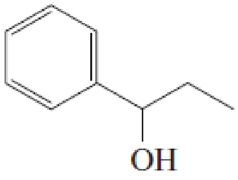
(a)  because the more stable carbocation intermediate is the benzylic

carbocation,  , which then reacts with a chloride ion.

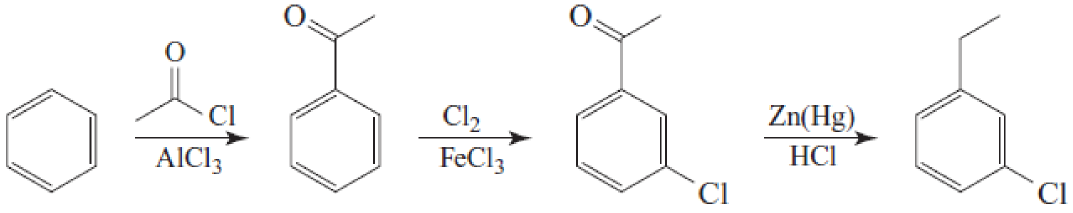
(b)  because the more stable intermediate is a mercurinium ion in which a partial positive charge resides on the benzylic carbon, which then reacts with H_2O.

14.15

(a) The first method would fail because introducing the chlorine substituent first would introduce an ortho-para directing group. Consequently, the subsequent Friedel-Crafts reaction would not then take place at the desired meta position.

The second method would fail for essentially the same reasons. Introducing the ethyl group first would introduce an ortho-para director, and subsequent ring chlorination would not take place at the desired meta position.

(b) If we introduce an acetyl group first, which we later convert to an ethyl group, we install a meta director. This allows us to put the chlorine atom in the desired position. Conversion of the acetyl group to an ethyl group is then carried out using the Clemmensen (or Wolff-Kishner) reduction.



14.16

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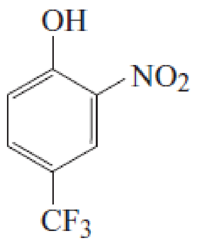
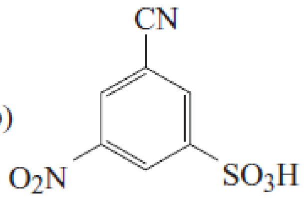
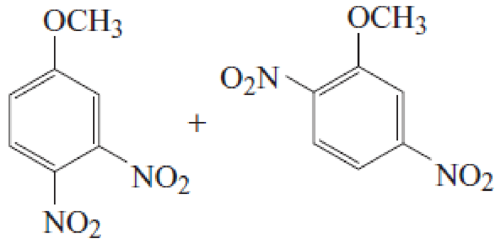
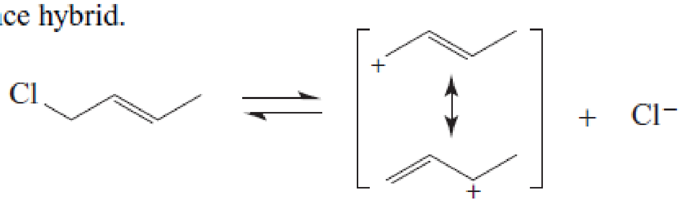
(a)  (b)  (c) 

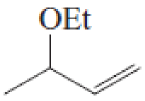
14.17

(a) In concentrated base and ethanol (a relatively nonpolar solvent), the S_N2 reaction is favored. Thus, the rate depends on the concentration of both the alkyl halide and ONa. Since no carbocation is formed, the only product is

(b) When the concentration of O^- ion is small or zero, the reaction occurs through the S_N1 mechanism. The carbocation that is produced in the first step of the S_N1 mechanism is a resonance hybrid.



This ion reacts with the nucleophile (O^- or OH) to produce two isomeric ethers

and 

14.18

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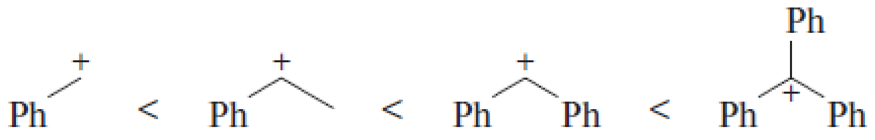
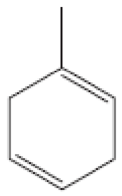
The relative rates are in the order of the relative stabilities of the carbocations:



The solvolysis reaction involves a carbocation intermediate.

14.19



Review Problems

Mechanisms

14.20

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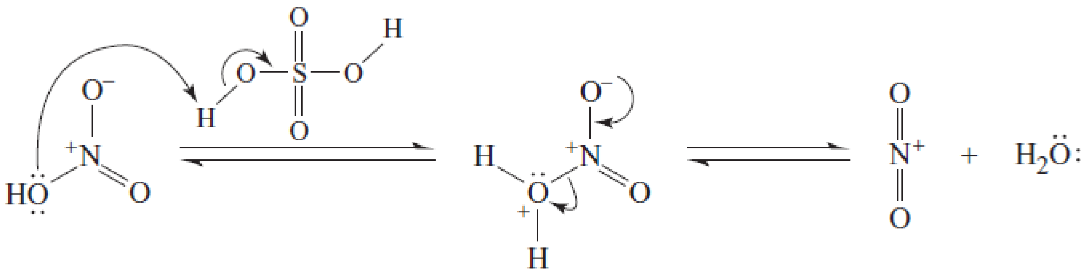
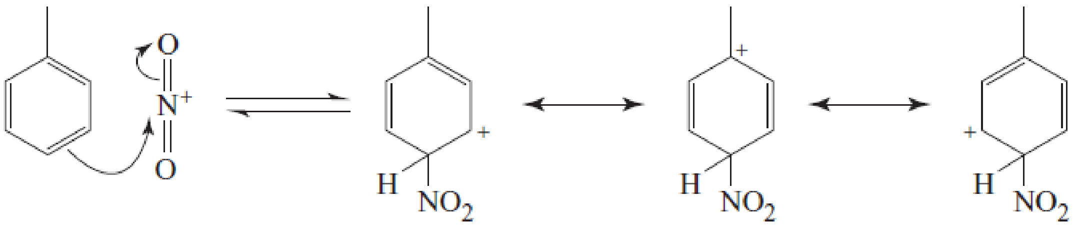
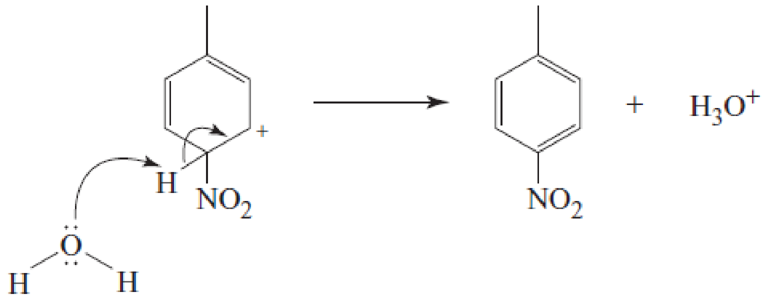
(a) 1. Generate the electrophile



2. Attack the electrophile with aromatic ring to form the sigma complex.



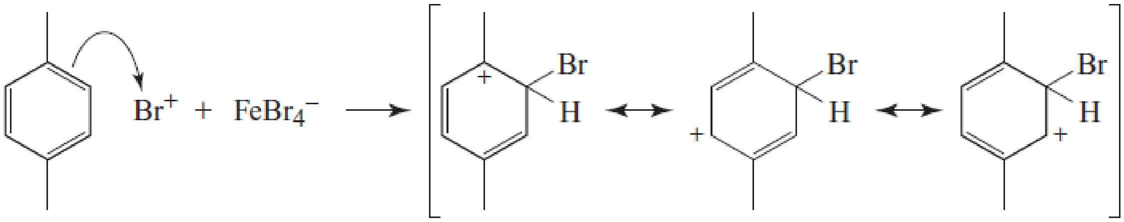
3. Elimination to regain aromaticity



(b) 1. Generate the electrophile

$$Br{-}Br + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$$

2. The aromatic ring attacks the electrophile to generate a resonance-stabilized sigma complex.



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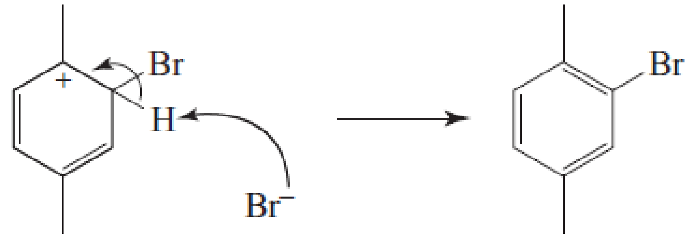
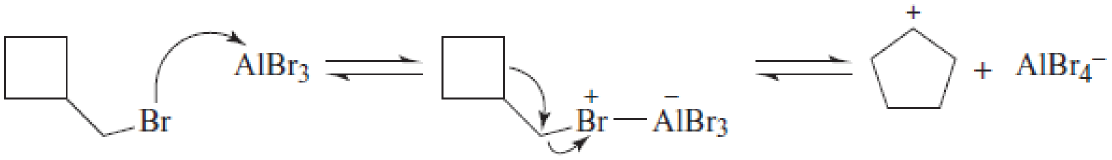
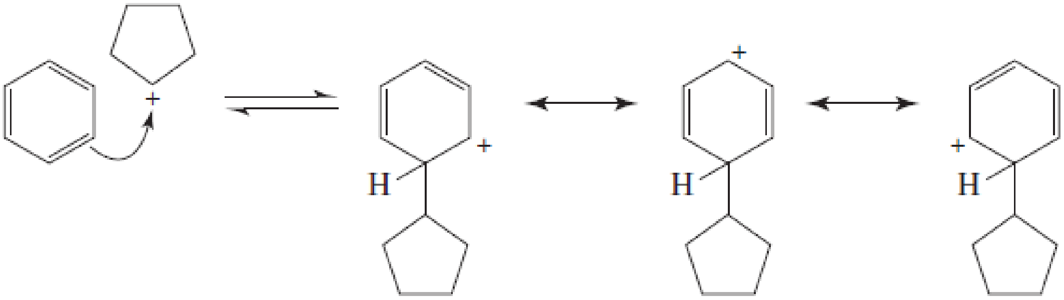
3. Elimination to regain aromaticity



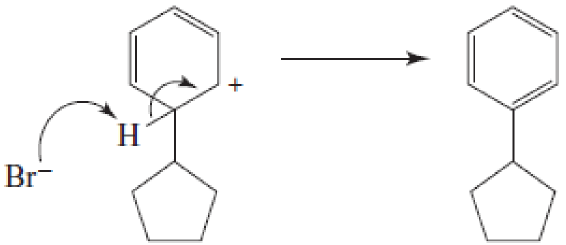
(c) 1. Generate the electrophile



2. Attack the electrophile with the aromatic ring to form the sigma complex.



3. Elimination to regain aromaticity



14.21

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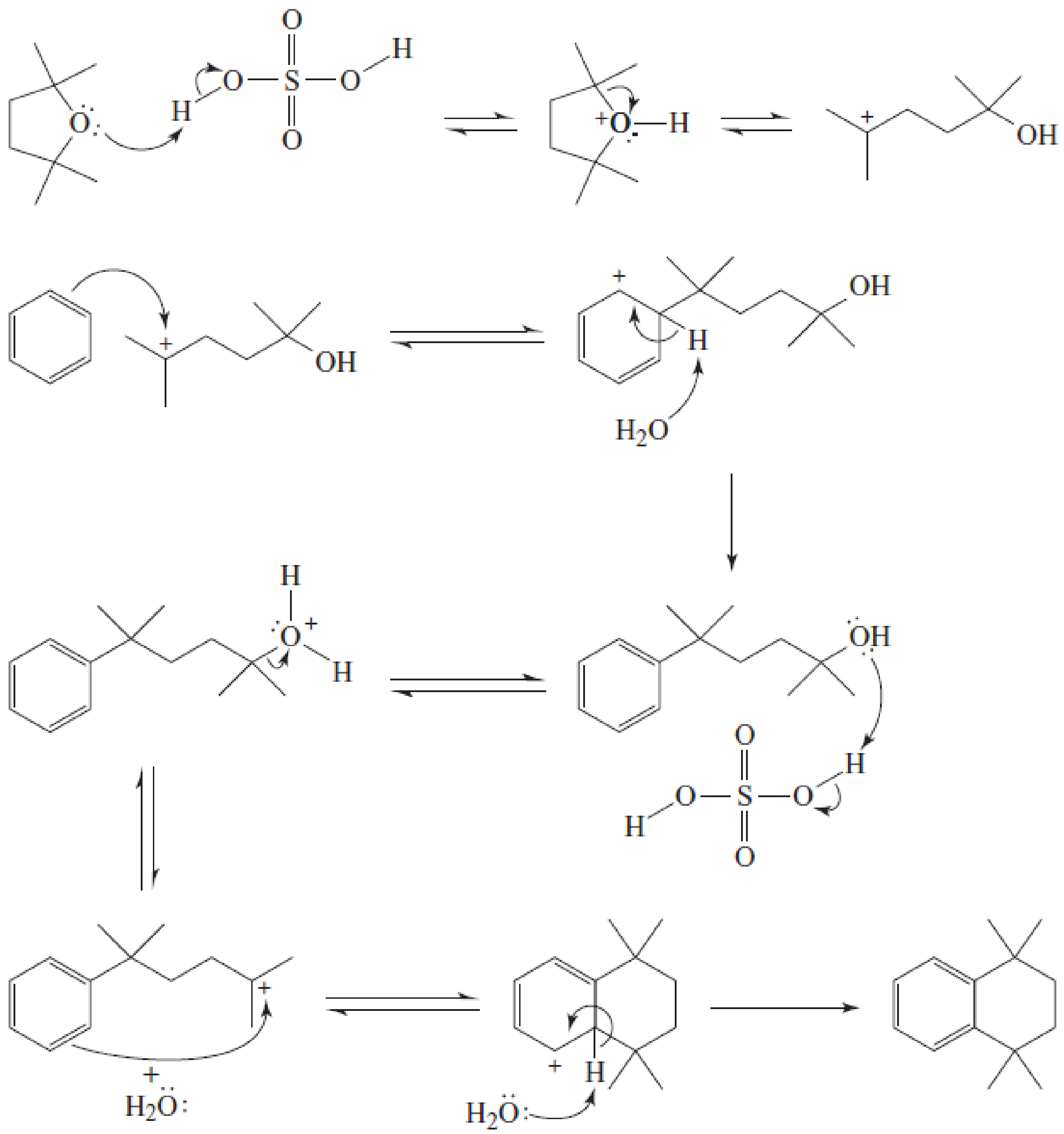

14.22

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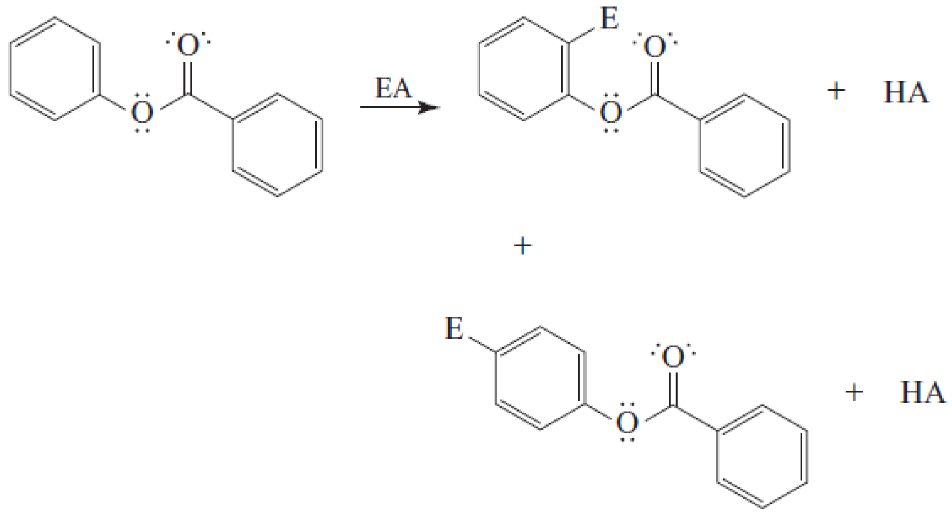
(a) Electrophilic aromatic substitution will take place as follows:



(b) The ring directly attached to the oxygen atom is activated toward electrophilic attack because the oxygen atom can donate an unshared electron pair to it and stabilize the intermediate arenium ion when attack occurs at the ortho or para position.

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14.23

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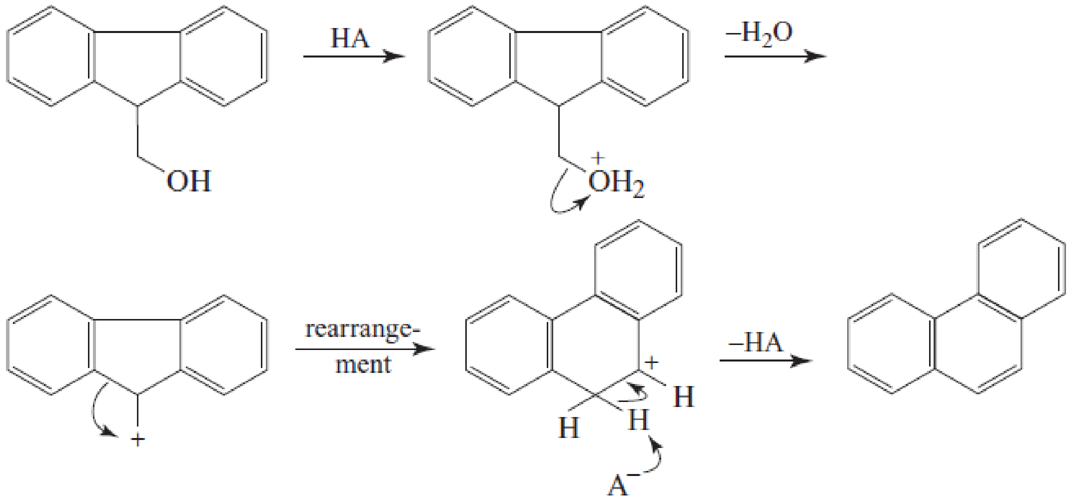
(a)



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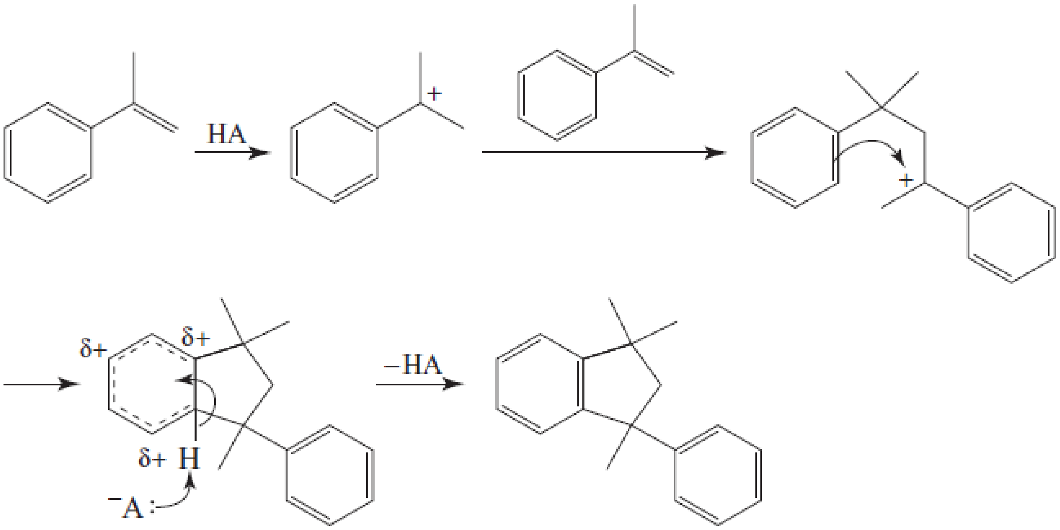

Reactions and Synthesis

14.24

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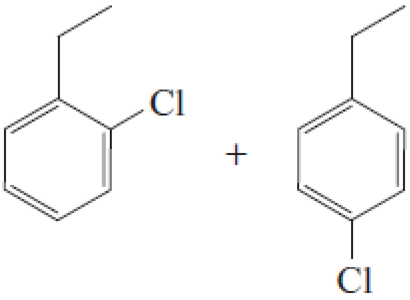
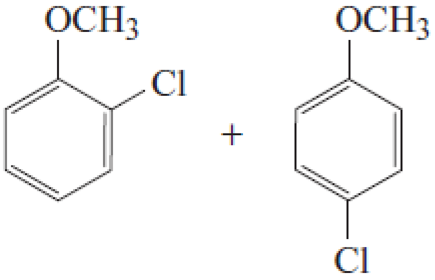
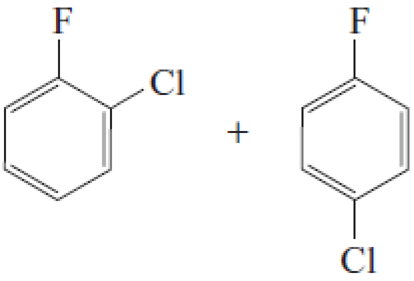
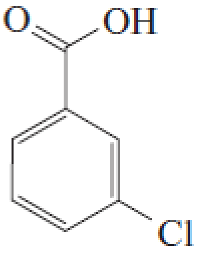
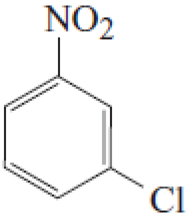
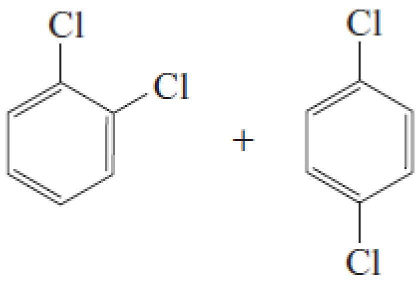
(a) 

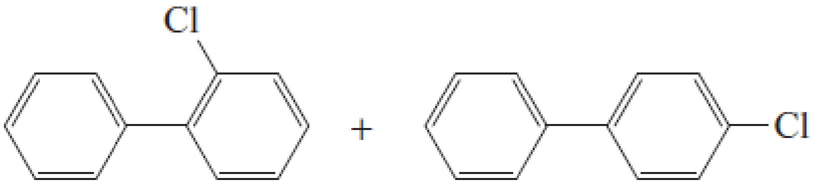
(b) 

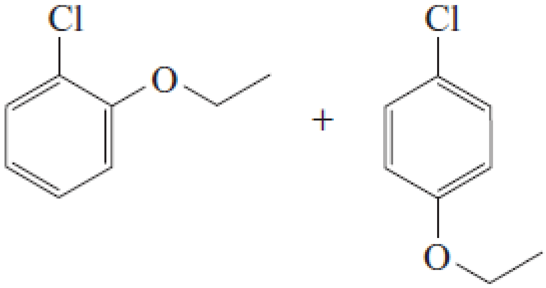
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

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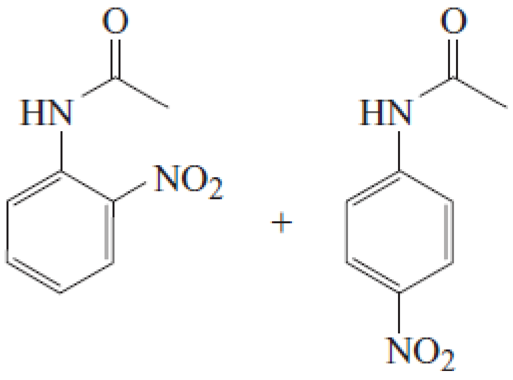
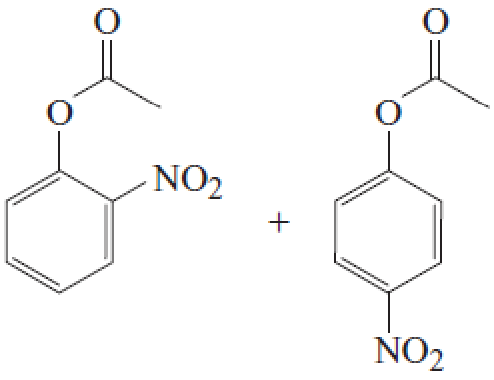
14.25

(a) 

(mainly)

(b) 

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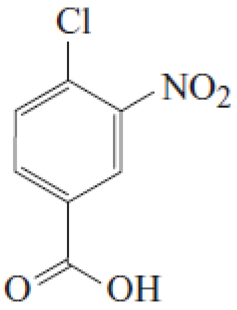
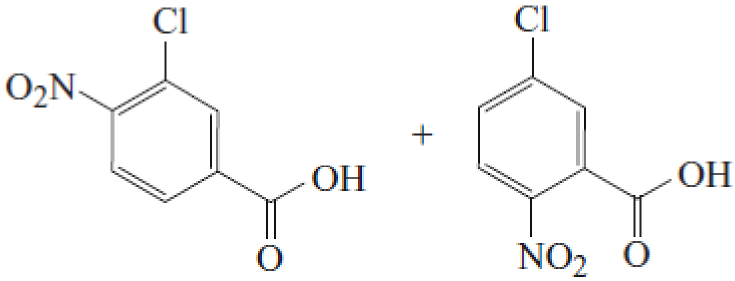
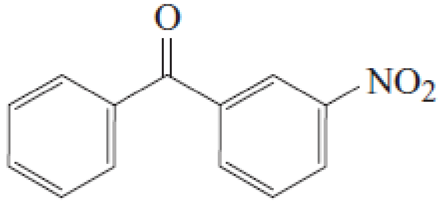
(c) 

(d) 

(e) 

14.26

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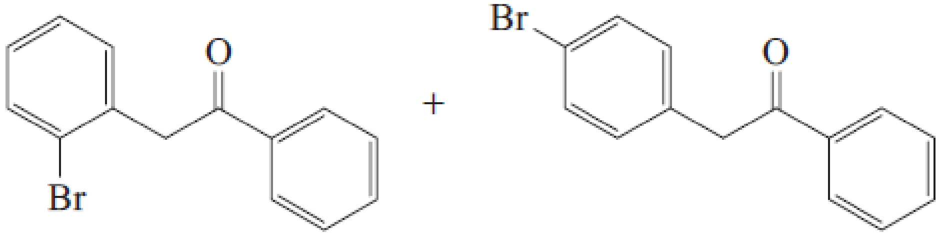
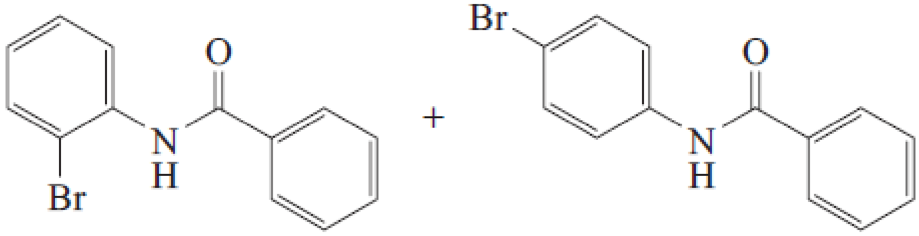
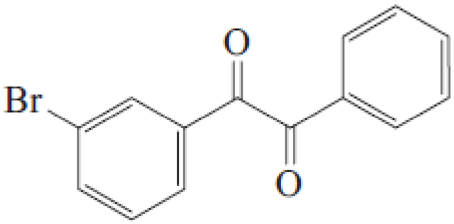
(a) 

(b) 

(c) 

14.27

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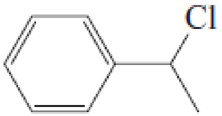
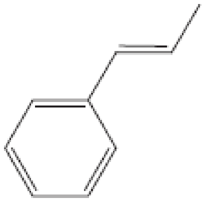
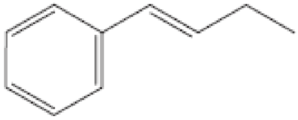
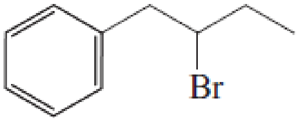
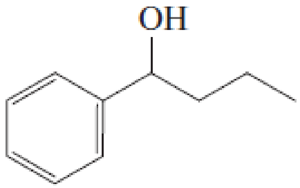
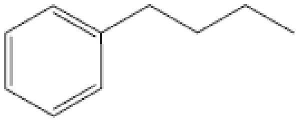
(a) 

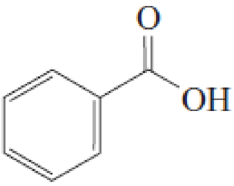
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

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14.28

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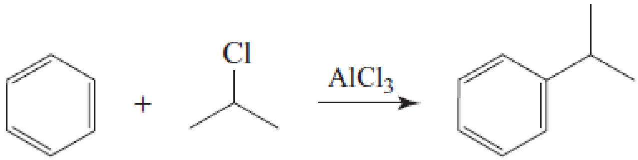
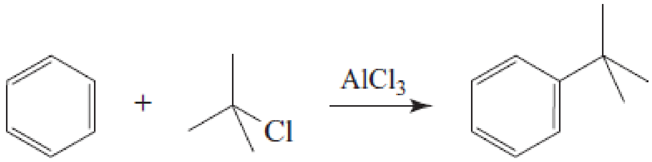
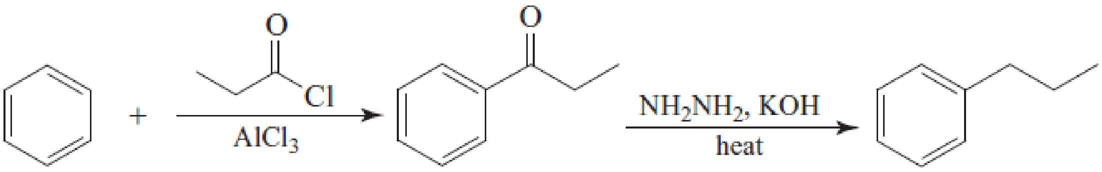
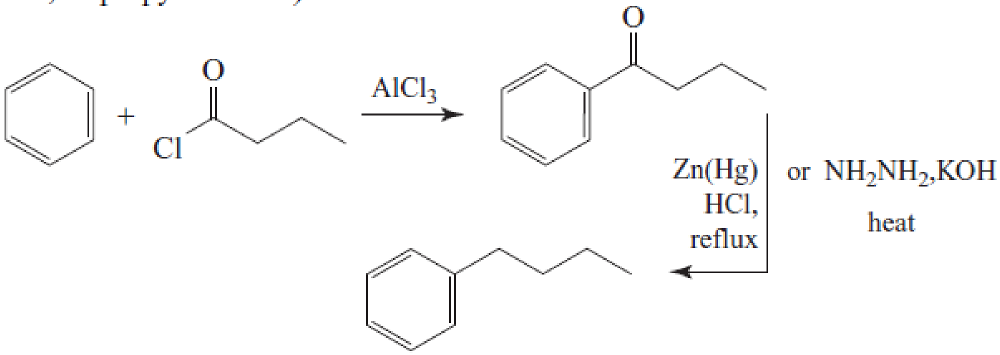
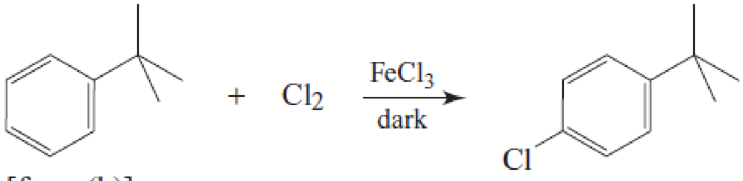
(a) 

(b) 

(c) 

(*Note:* The use of Cl in a Friedel-Crafts synthesis gives mainly the rearranged product, isopropylbenzene.)

(d) 

(e) 

[from (b)]

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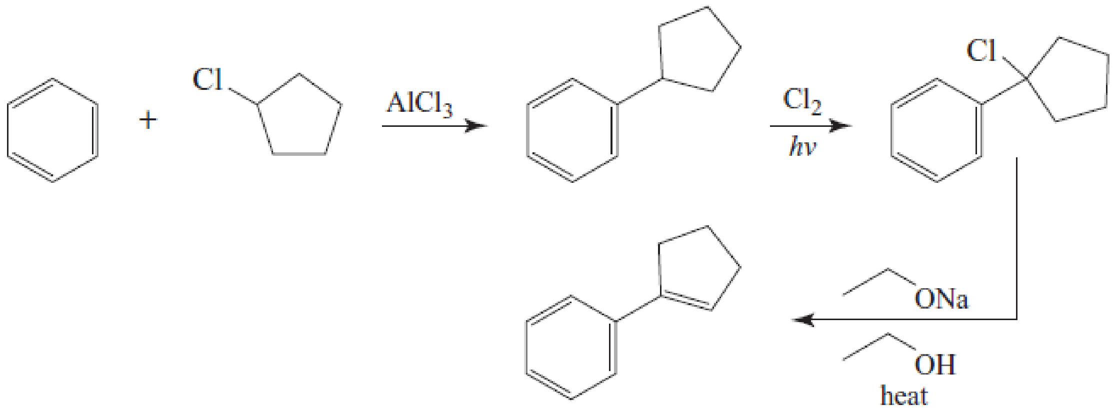
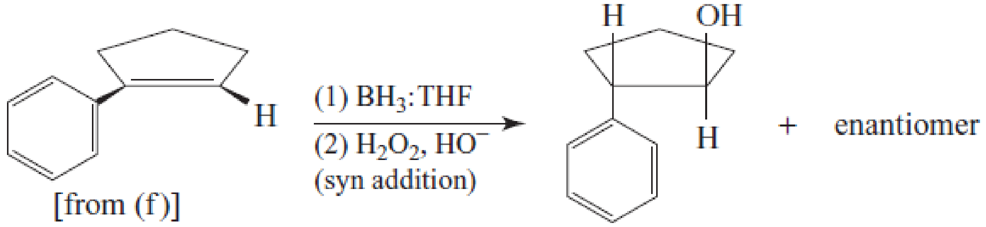
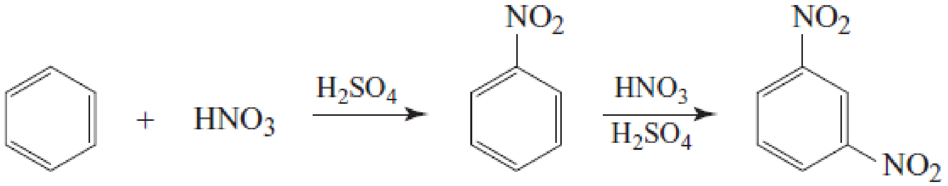
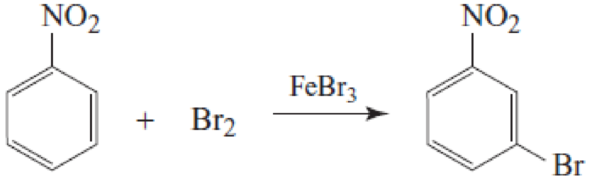
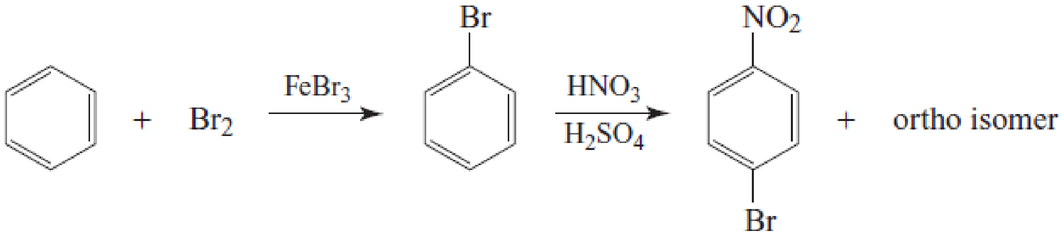
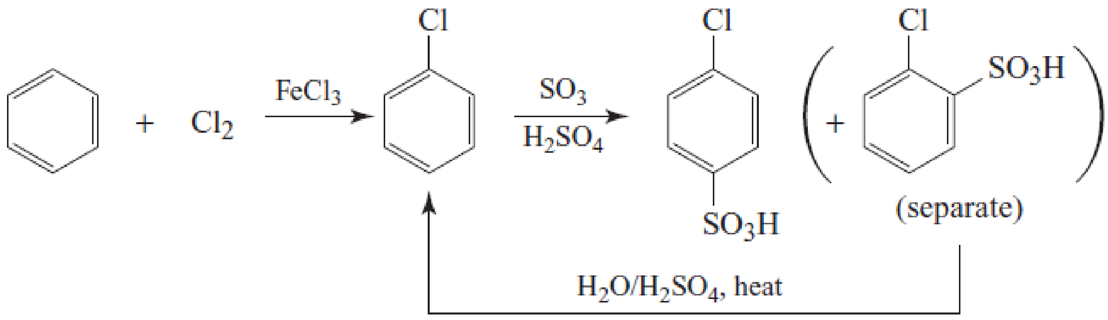
(f) 
Cl
AlCl3
Cl2
hv
Cl
ONa
OH
heat

(g) 
H
[from (f)]
(1) BH3:THF
(2) H2O2, HO−
(syn addition)
H
OH
H
+ enantiomer

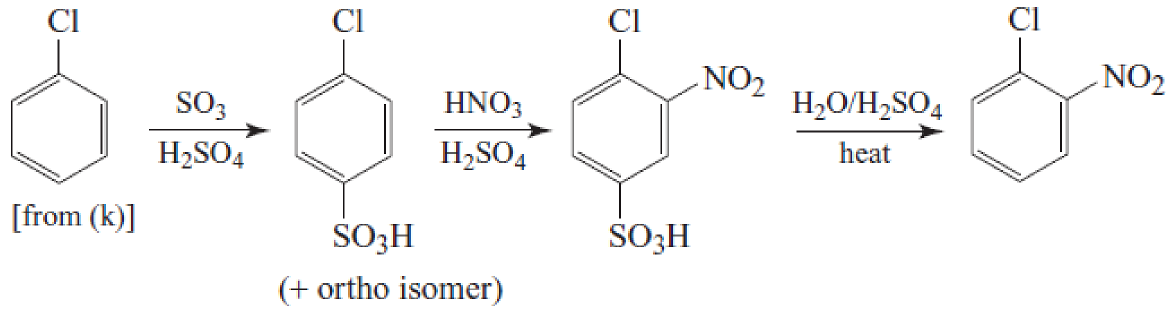
(h) 
+ HNO3
H2SO4
NO2
HNO3
H2SO4
NO2
NO2

(i) 
NO2
+ Br2
FeBr3
NO2
Br

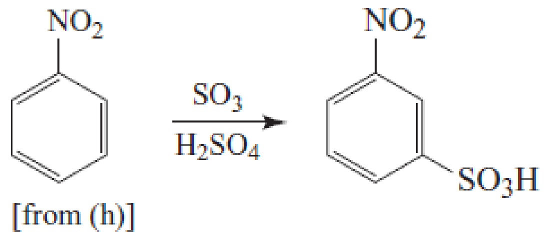
(j) 
+ Br2
FeBr3
Br
HNO3
H2SO4
NO2
Br
+ ortho isomer

(k) 
+ Cl2
FeCl3
Cl
SO3
H2SO4
Cl
SO3H
Cl
SO3H
(separate)
H2O/H2SO4, heat

(l)



(m)



14.29

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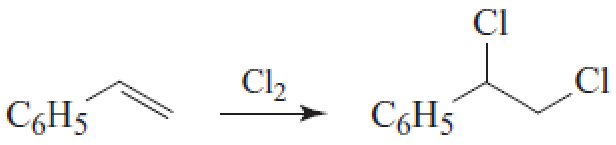
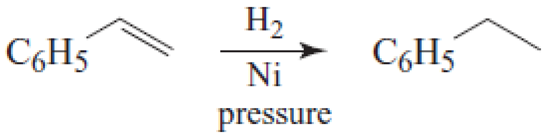
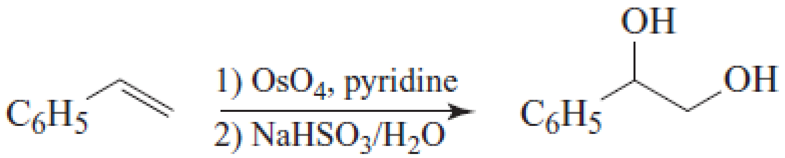
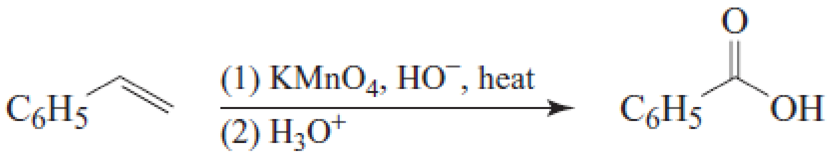
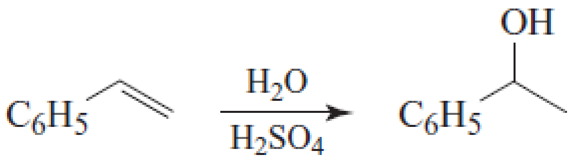
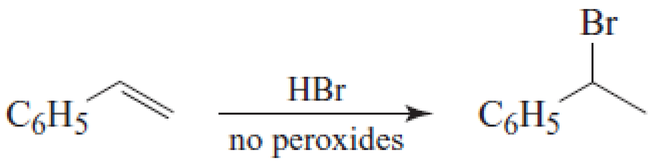
(a) 

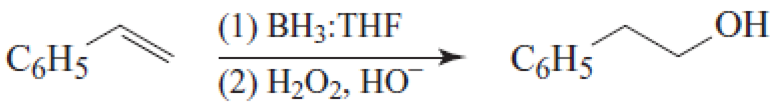
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

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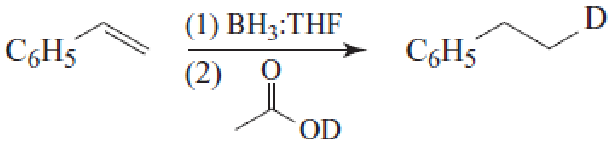
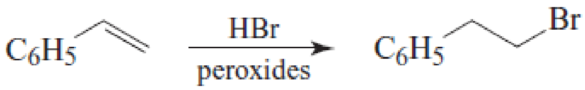
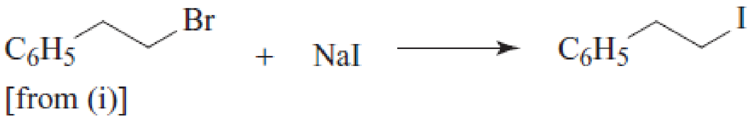
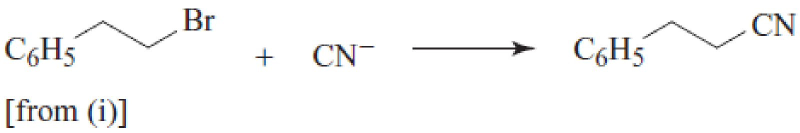
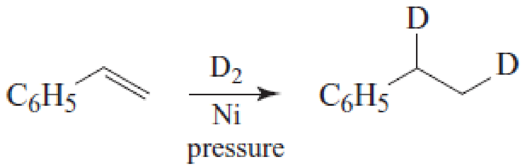
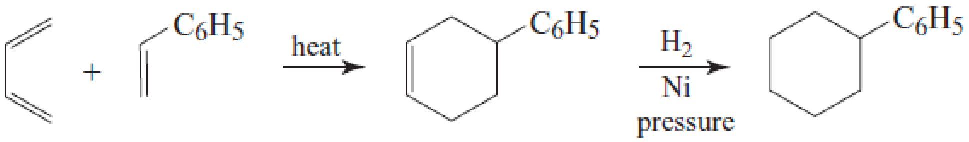
(h) 

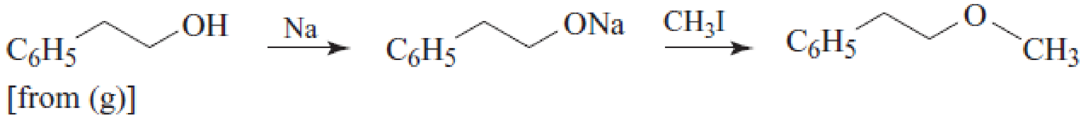
(i) 

(j) 

(k) 

(l) 

(m) 

(n) 

14.30

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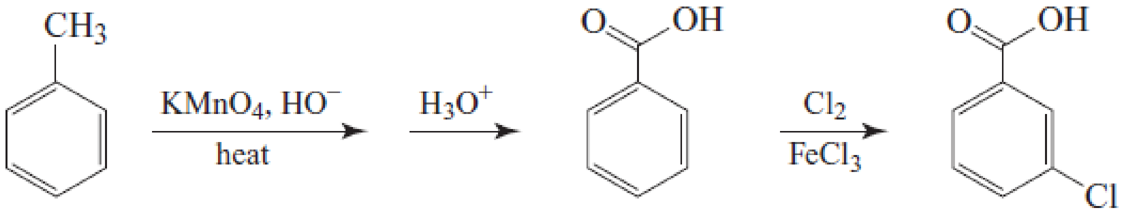
(a)



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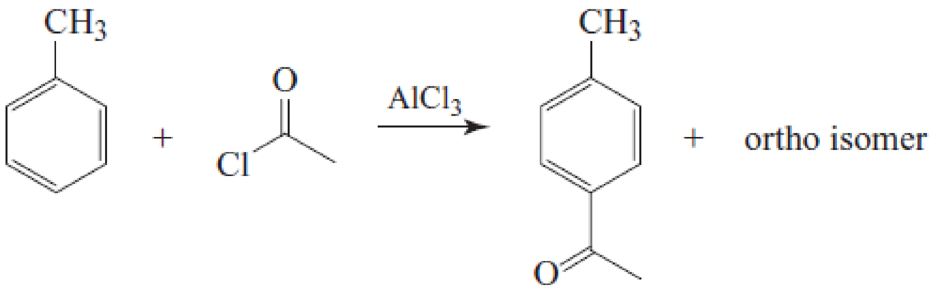

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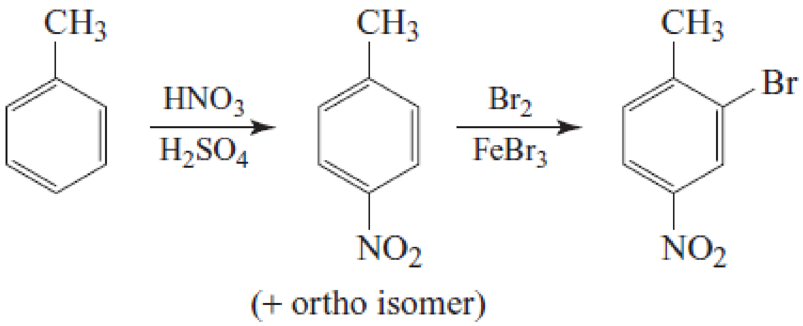

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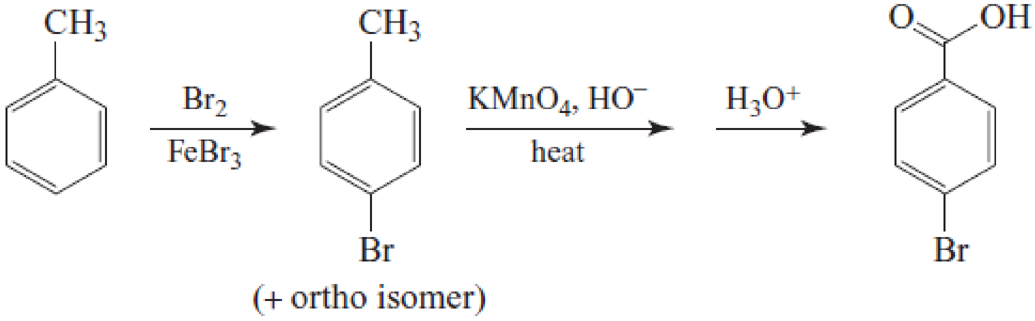

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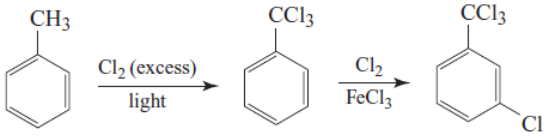
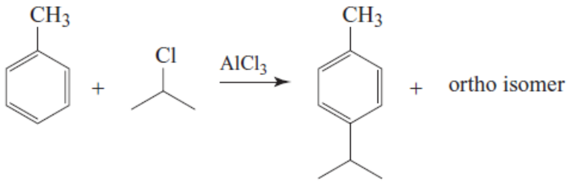
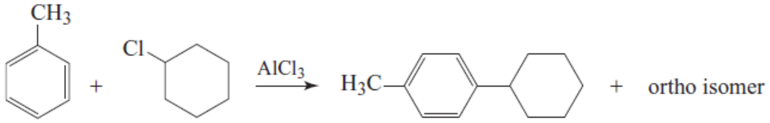
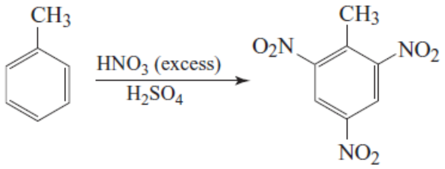
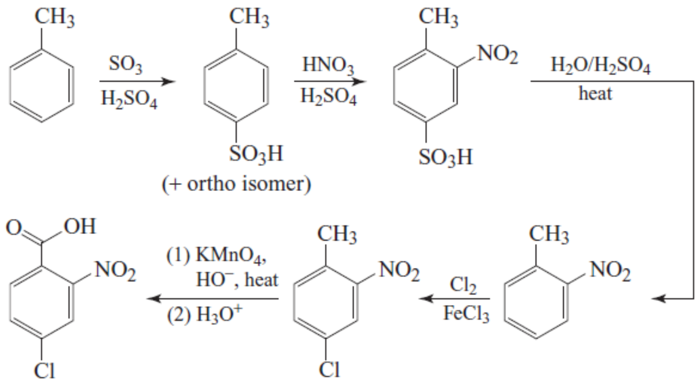
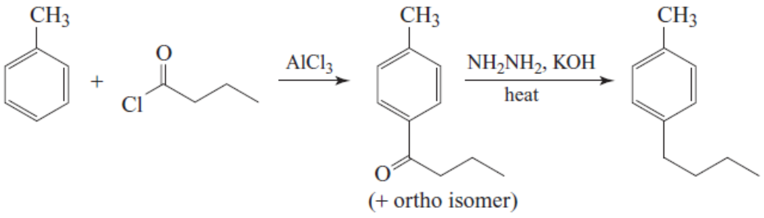
(e) 

(f) 

(g) 

(h) 

(i) 

(j) 

14.31

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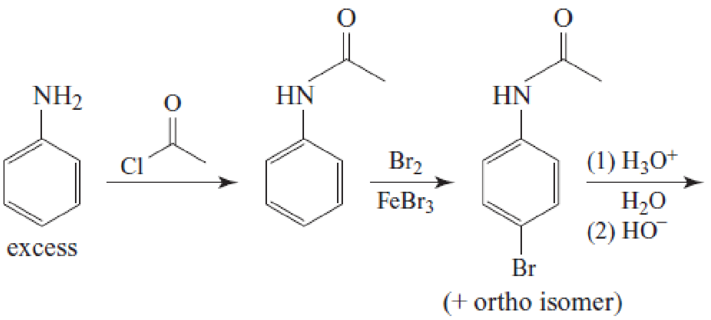
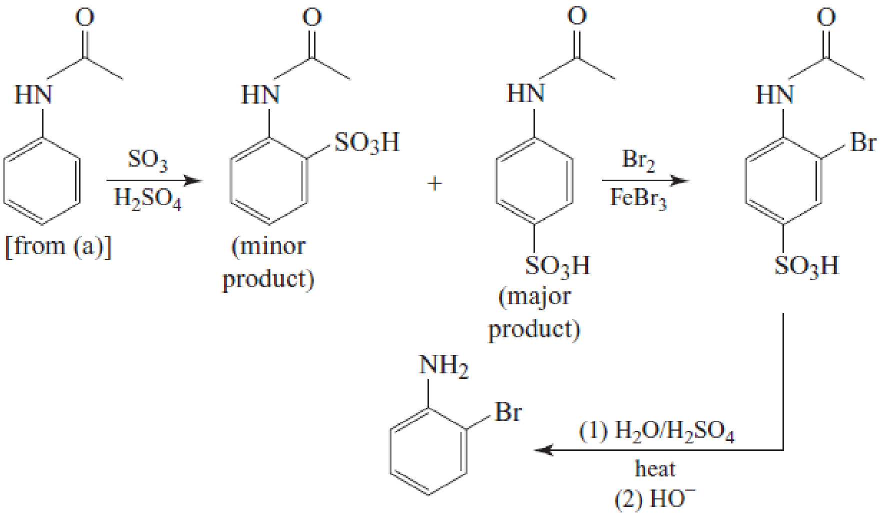
(a)



(b)



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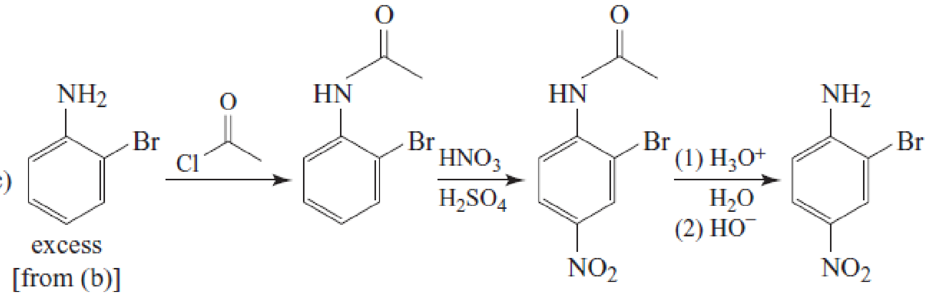

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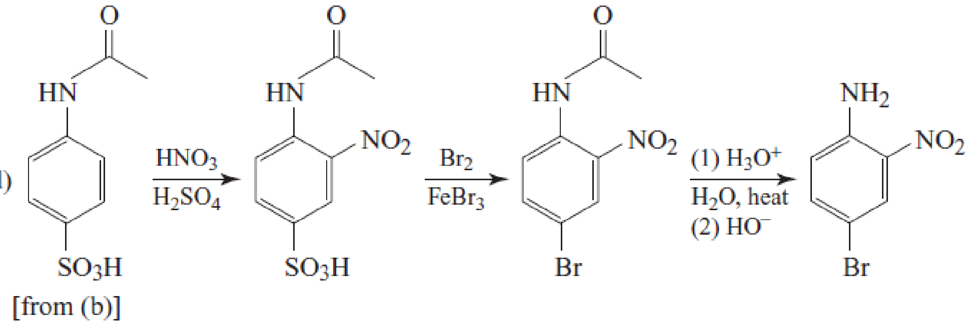

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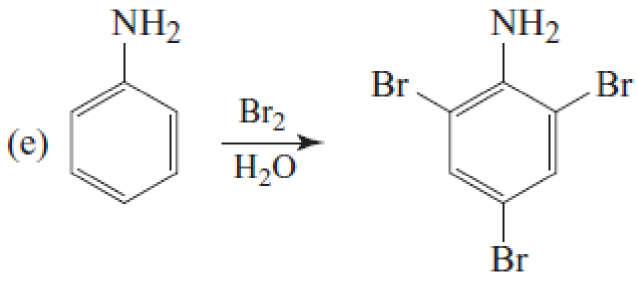
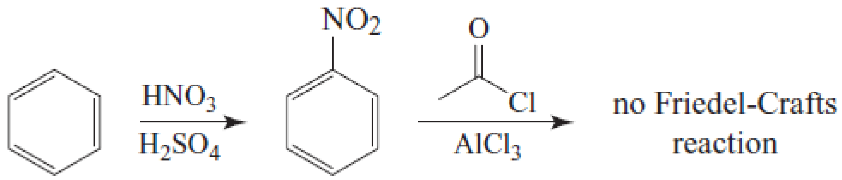
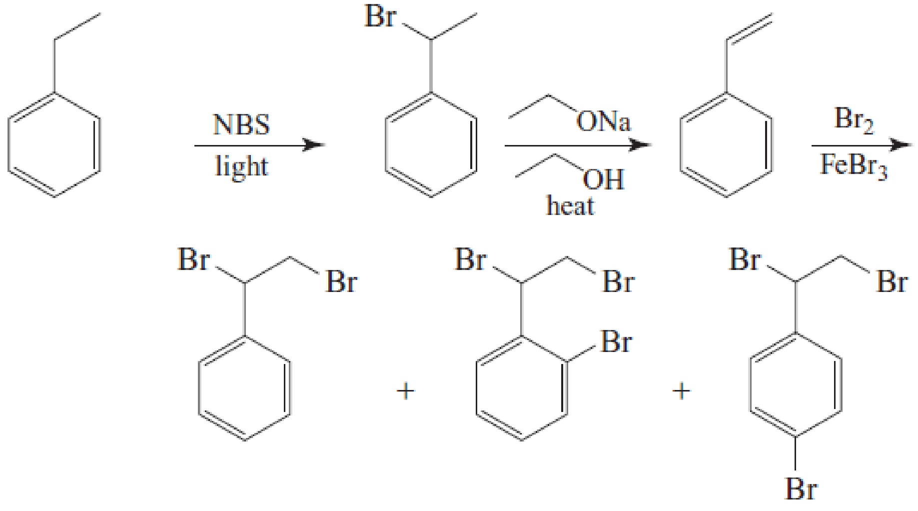


14.32

(a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an —NO_2 group (or any meta director).



(b) The last step will first brominate the double bond.



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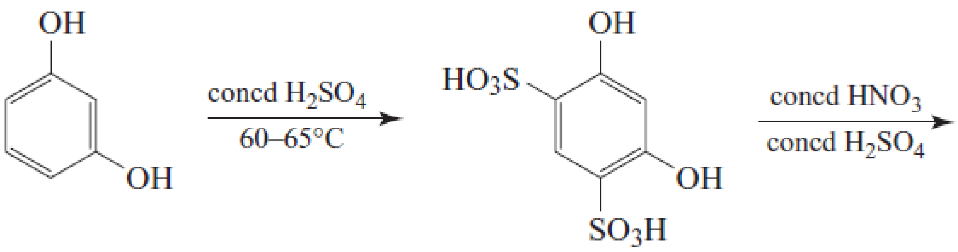
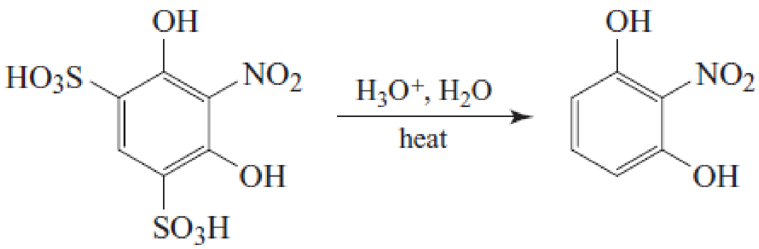
This problem serves as another illustration of the use of a sulfonic acid group as a blocking group in a synthetic sequence. Here we are able to bring about nitration between two meta substituents.



G



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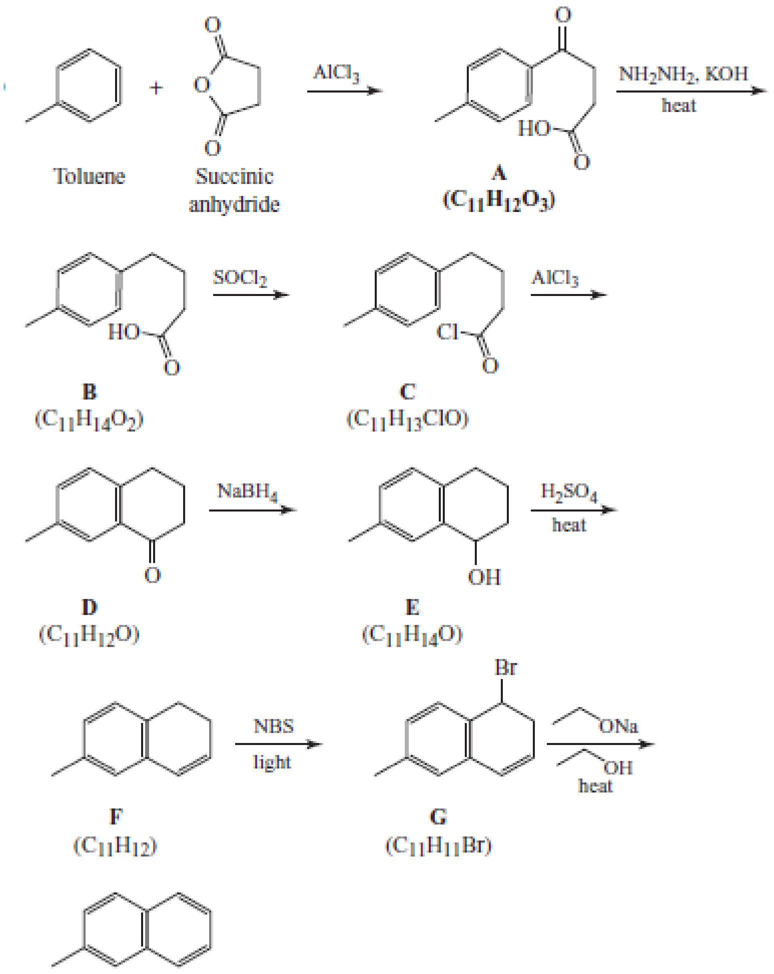
14.34



2-Methylnaphthalene

General Problems

14.35

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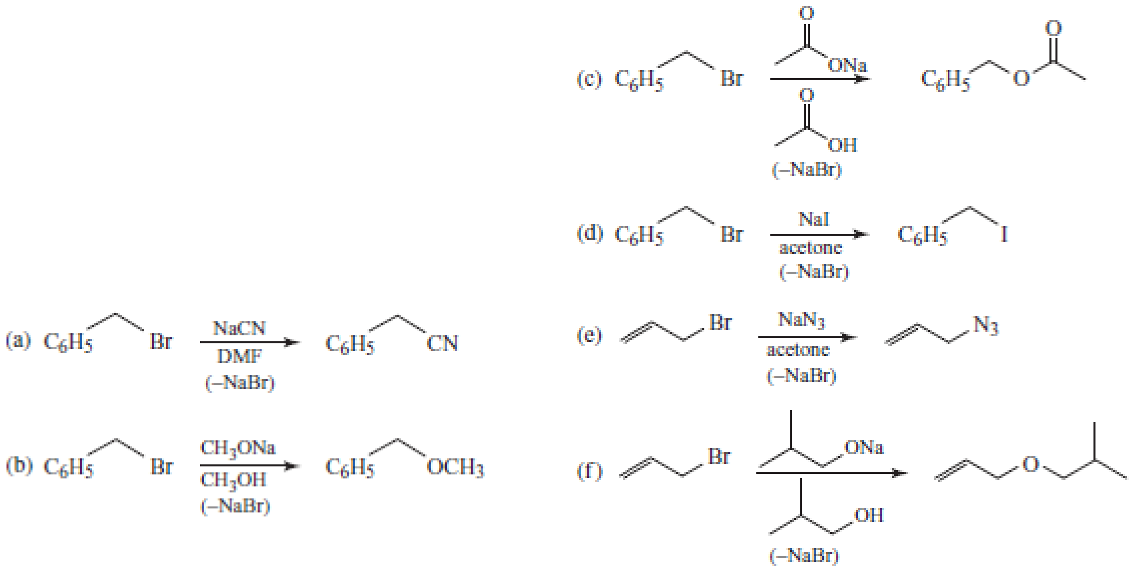

14.36

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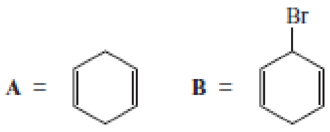

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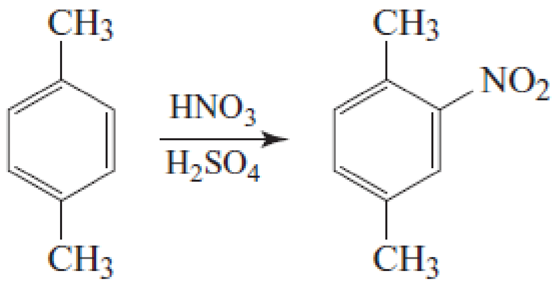

(only possible mononitro product)

14.38

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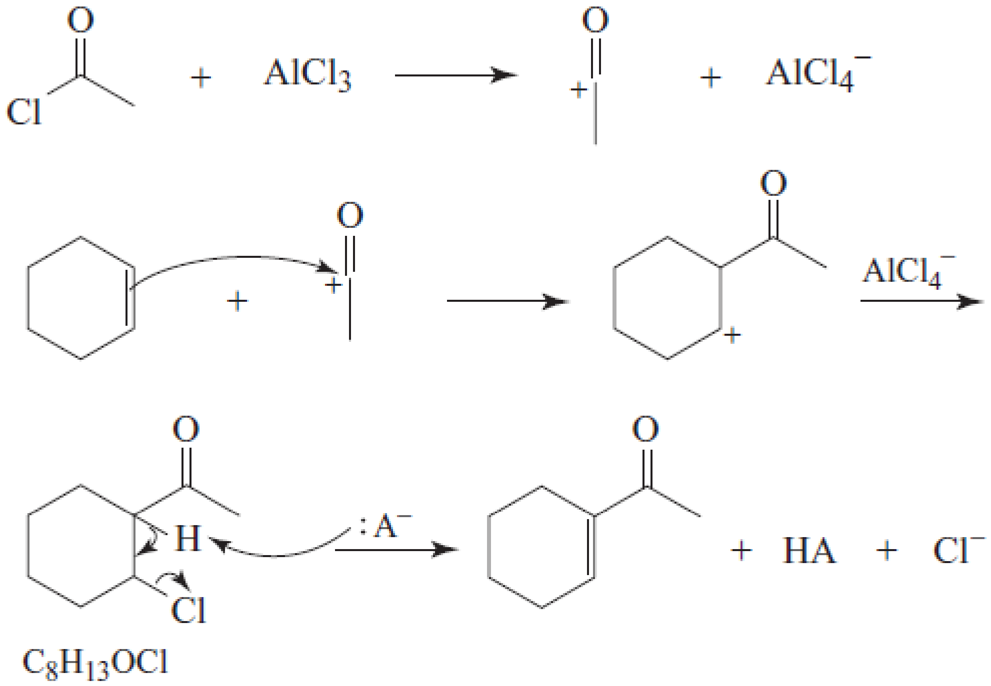

14.39

(a and b) The *tert*-butyl group is easily introduced by any of the variations of the Friedel-Crafts alkylation reaction, and, because of the stability of the *tert*-butyl cation, it is easily removed under acidic conditions.

(c) In contrast to the $-SO_3H$ group often used as a blocking group, $-C(CH_3)_3$ activates the ring to further electrophilic substitution.

14.40

The evidence indicates that the mechanistic step in which the C—H bond is broken is *not* rate determining. (In the case cited, it makes no difference kinetically if a C—H or C—D bond is broken in electrophilic aromatic substitution.) This evidence is consistent with the two-step mechanism given in Section 15.2. The step in which the aromatic compound reacts with the electrophile (NO_2^+) is the slow rate-determining step. Proton (or deuteron) loss from the arenium ion to return to an aromatic system is a rapid step and has no effect on the overall rate.

14.41

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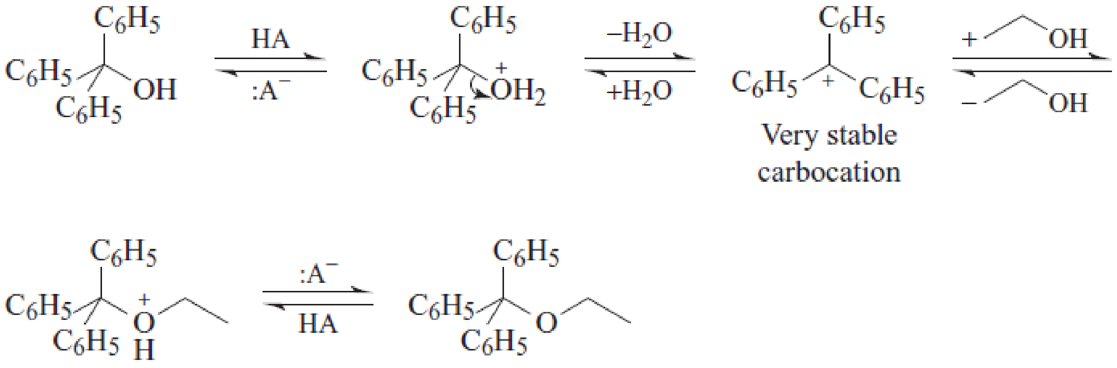
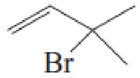


14.42

(a) would be the most reactive in an S_N2 reaction because it is a 1° allylic halide. There would, therefore, be less steric hindrance to the attacking nucleophile.

(b)  would be the most reactive in an S_N1 reaction because it is a 3° allylic halide. The carbocation formed in the rate-determining step, being both 3° and allylic, would be the most stable.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. **(b)** More the electron density on ring (due to electron donating effect of OH by +M), more is the rate of reaction with electrophile.

2. **(d)** Less the electron density on benzene ring (due to electron withdrawing effect of nitro by -M), less is the rate of electrophilic aromatic substitution.

3. **(d)** Methyl group of toluene is o/p directing.

4. **(d)** It is electrophilic substitution reaction.

5. **(c)** More the electron density on ring, more is the rate of reaction with electrophile.

6. **(b)** Methyl is o/p directing while nitro is m directing in EAS.

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7. **(c)** Less the electron density on benzene ring (due to electron withdrawing effect of nitro by -M), less is the rate of electrophilic aromatic substitution.

8. **(a)** A is ethyne, B is benzene, C is toluene formed by Friedel Crafts Alkylation.

9. **(a)** It acts as a base and releases hydroxide ion.

10. **(b)** Nitration will take place at m position of deactivating carboxylic group.

11. **(c)** Nitration (EAS) will take place at o/p with respect to activating group and m with respect to deactivating group.

12. (b) Vinyl carbocation is highly unstable, thus is not used in Friedel Crafts Alkylation.

13. (d) Left ring is more activated towards EAS due to +M effect of N.

14. (d) Rearrangement is possible in Friedel Crafts Alkylation as carbocation is formed as an intermediate.

15. (b) I^+ will act as electrophile in the interhalogen molecule.

16. (b) Nitration (EAS) will yield para product as the major product.

17. **(d)** X is 3-chloropropene and Y is $KMnO_4$, H^+, Δ.

18. (b) The ring is activated towards EAS due to +M of N.

19. **(d)** We require EtCl + $AlCl_3$, NBS + Δ, alc. KOH.

20. **(c)** Major product will be para for the EAS reaction.

21. **(c)** EAS will take place at o/p with respect to activating group.

22. **(a)** More the electron density on ring, more is the rate of EAS.

23. **(c)** EAS will take place with the carbonyl carbon as electrophile (Friedel Crafts Acylation).

24. **(c)** All three H of methyl will be substituted by Cl and then the EAS will take place at m position of deactivating trichloromethyl group.

25. **(c)** It generates electrophile.

27. **(b)** It is an octet complete carbocation stabilized by resonance with lone pair of adjacent O atom.

28. **(c)** EAS will take place at o/p with respect to activating group and m with respect to deactivating group.

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29. **(a)** In P, diazonium is formed at the position of amine, in Q OH group substituted diazonium while R is formed by Riemer Tiemann Reaction of Q.

30. (d) Phenol will be formed first due to hydrolysis with acid and then the carbocation will give EAS reaction on phenol at the para position.

<H2> Linked Comprehension Type

1. **(b)** N is a stronger activating group for EAS than O, thus EAS takes place with respect to it.

2. **(d)** More the electron density on ring, more is the rate of EAS.

3. **(a)** Nitrogen with its lone pair is electron donating group and thus o/p directing.

<H2> Matrix Match Type

1. $a \rightarrow (p, r); b \rightarrow (p, r); c \rightarrow (p, r); d \rightarrow (p, r)$

EAS will take place at o/p with respect to activating electron donating group and m with respect to deactivating electron withdrawing group.

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2. $a \rightarrow (p, r); b \rightarrow (p, r); c \rightarrow (p, r); d \rightarrow (p, s)$

EAS will take place at o/p with respect to activating electron donating group and m with respect to deactivating electron withdrawing group. More the electron density on ring, more is the rate of EAS.

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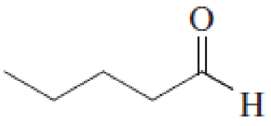
Chapter 15: Aldehydes and Ketones I: Nucleophilic Addition to the Carbonyl Group

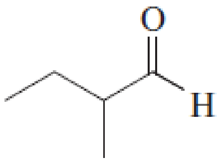
Practice Problems

15.1

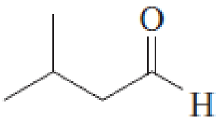
(a)



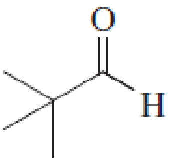
Pentanal



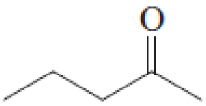
2-Methylbutanal



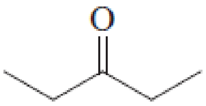
3-Methylbutanal



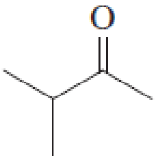
2,2-Dimethylpropanal



2-Pentanone



3-Pentanone



3-Methyl-2-butanone

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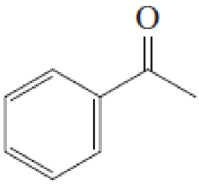
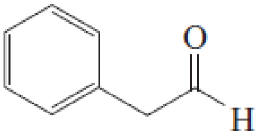
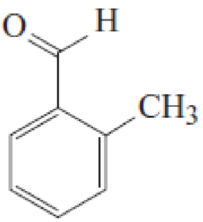
(b)



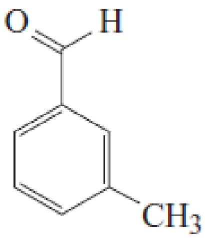
Acetophenone
(methyl phenyl ketone)



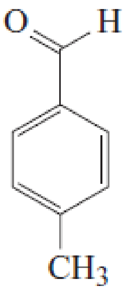
Phenylethanal
(phenylacetaldehyde)



2-Methylbenzaldehyde
(*o*-tolualdehyde)



3-Methylbenzaldehyde
(*m*-tolualdehyde)



4-Methylbenzaldehyde
(*p*-tolualdehyde)

15.2

(a) 1-Pentanol, because its molecules form hydrogen bonds to each other.

(b) 2-Pentanol, because its molecules form hydrogen bonds to each other.

(c) Pentanal, because its molecules are more polar.

(d) 2-Phenylethanol, because its molecules form hydrogen bonds to each other.

(e) Benzyl alcohol because its molecules form hydrogen bonds to each other.

15.3

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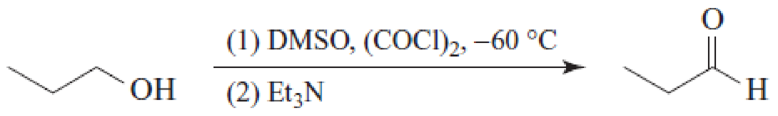
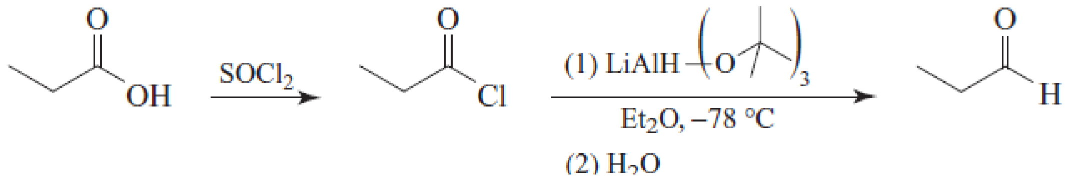
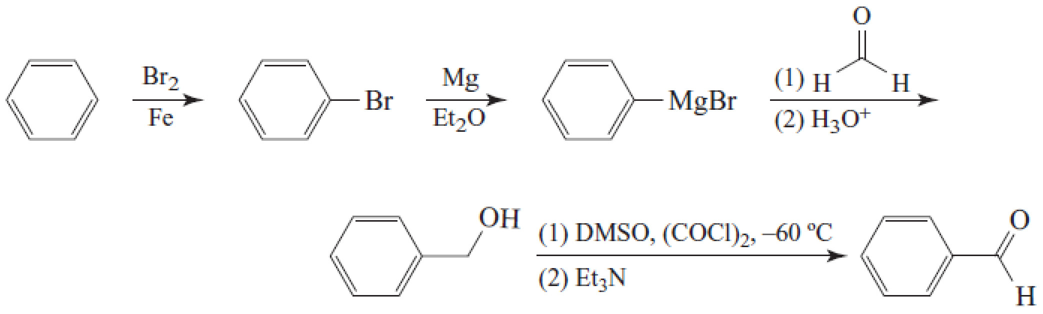
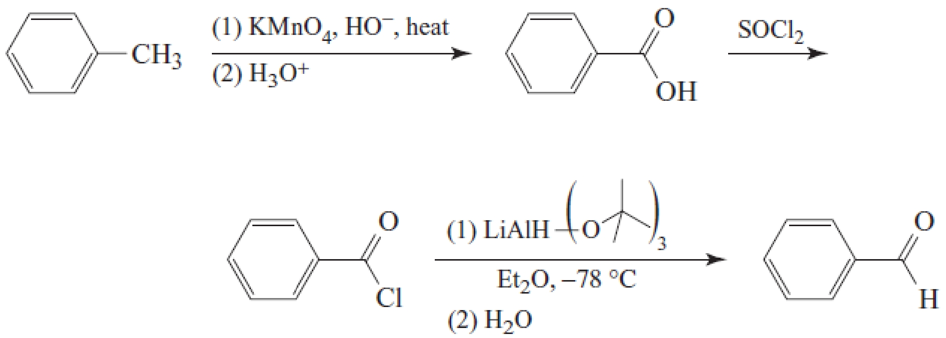
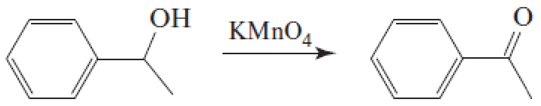
(a)

(1) DMSO, (COCl)2, −60 °C
(2) Et3N
OH
O
H

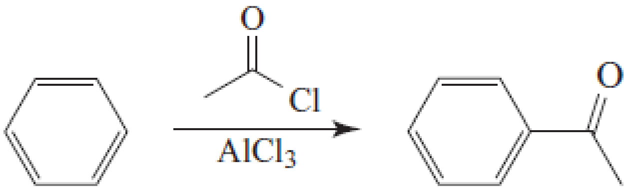
(b)

SOCl2
(1) LiAlH
Et2O, −78 °C
(2) H2O
OH
Cl
H

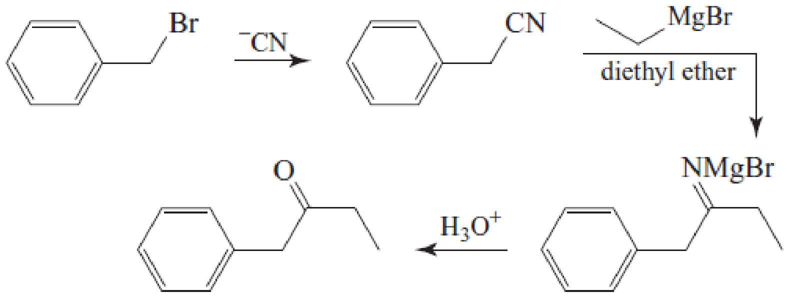
15.4

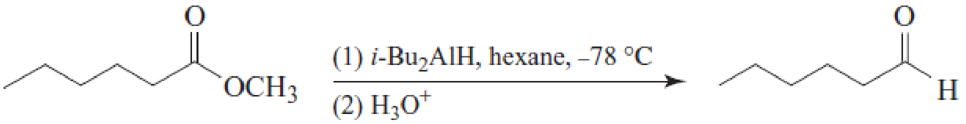
(a)

Br2
Fe
Br
Mg
Et2O
MgBr
(1) H H
(2) H3O+
OH
(1) DMSO, (COCl)2, −60 °C
(2) Et3N
H

(b)

CH3
(1) KMnO4, HO−, heat
(2) H3O+
OH
SOCl2
Cl
(1) LiAlH
Et2O, −78 °C
(2) H2O
H

(c)

OH
KMnO4
O

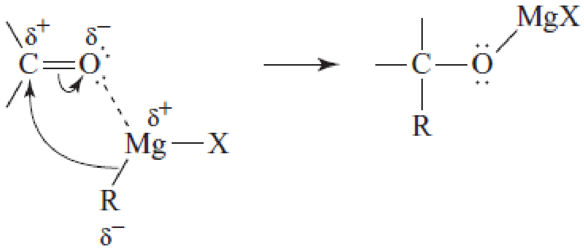
(d) 

(e) 

(f) 

15.5

(a) The nucleophile is the negatively charged carbon of the Grignard reagent *acting as a carbanion.*
(b) The magnesium portion of the Grignard reagent acts as a Lewis acid and accepts an electron pair of the carbonyl oxygen. This acid-base interaction makes the carbonyl carbon even more positive and, therefore, even more susceptible to nucleophilic attack.



(c) The product that forms initially (above) is a magnesium alkoxide salt.
(d) On addition of water, the organic product that forms is an alcohol.

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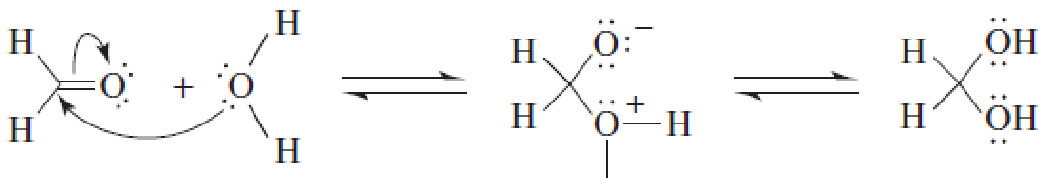
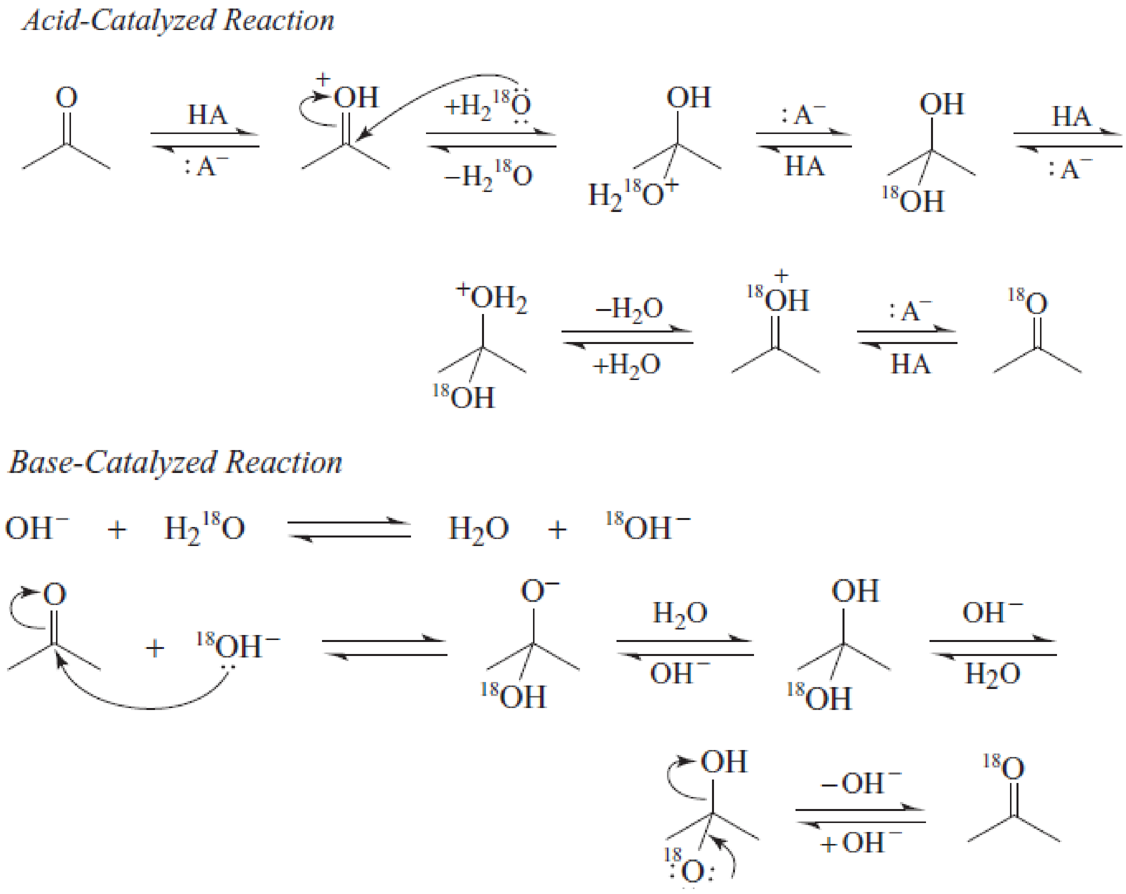
15.6

The nucleophile is a hydride ion.

15.7



15.8



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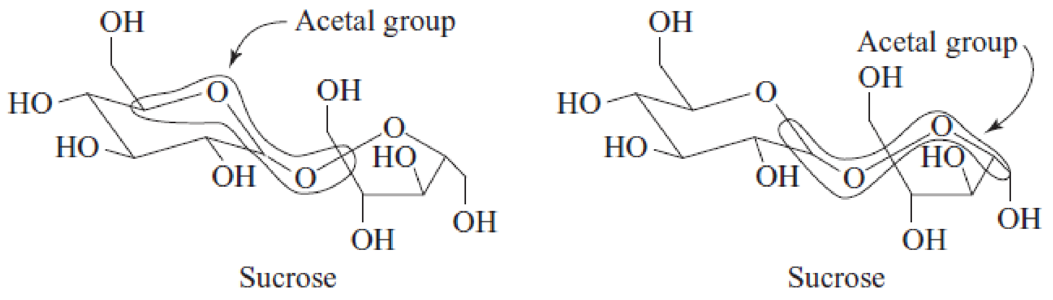

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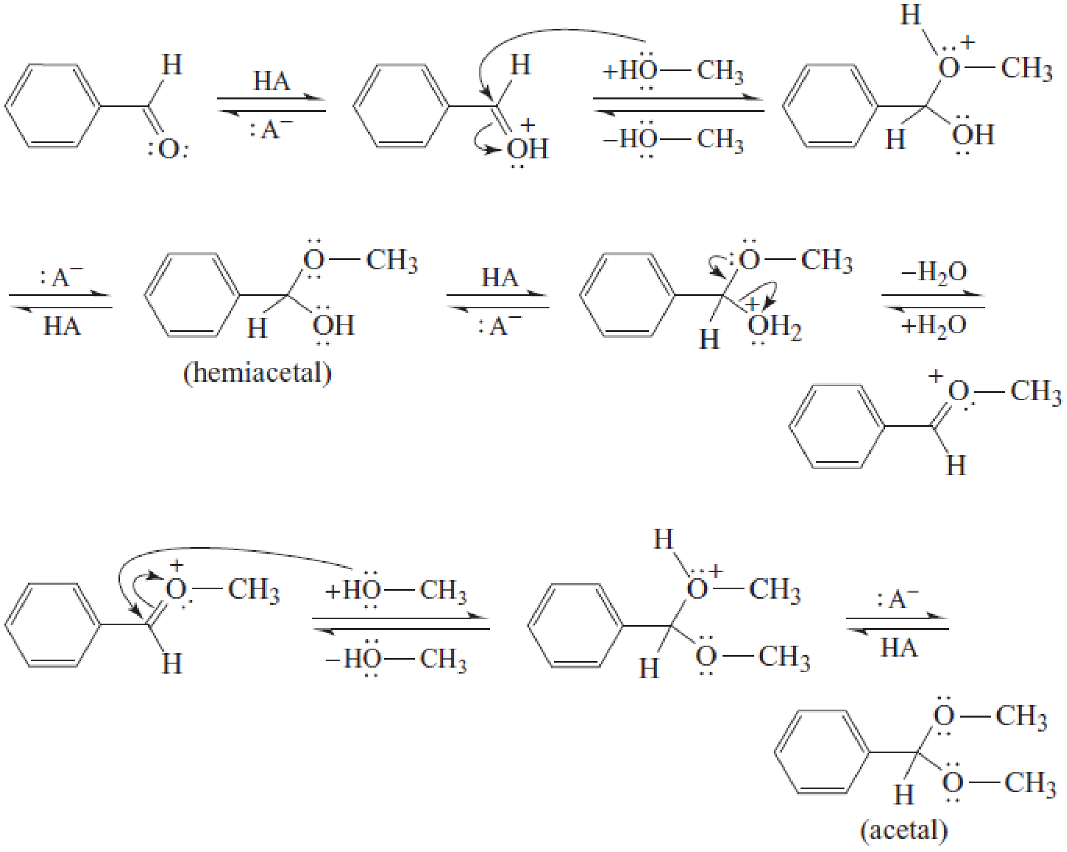

15.11

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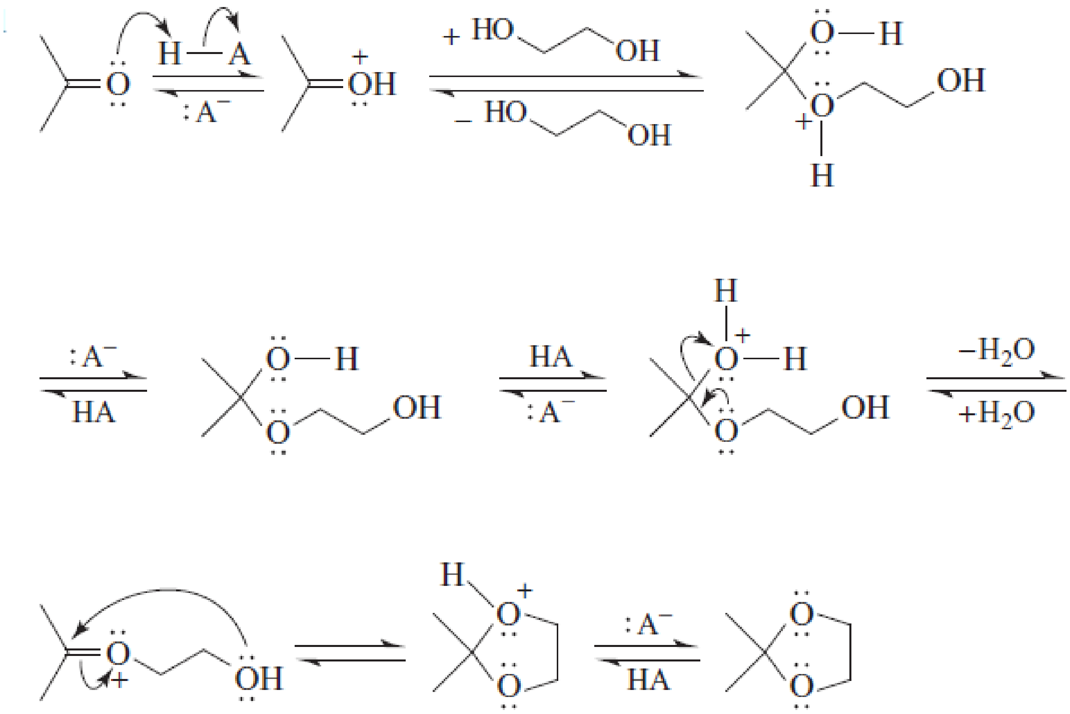

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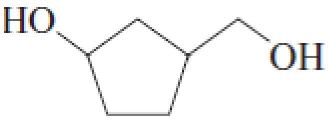
15.12



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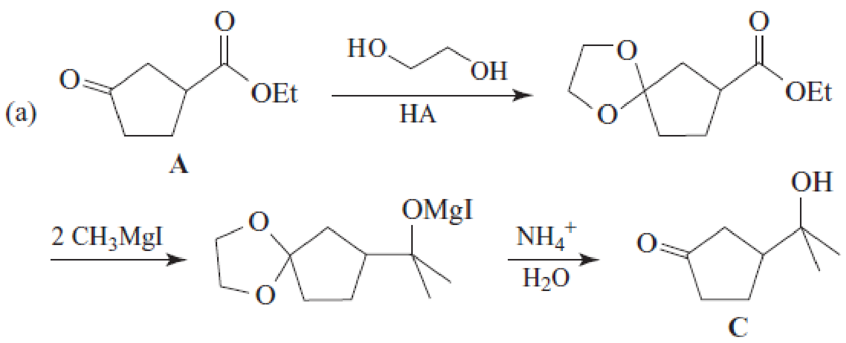
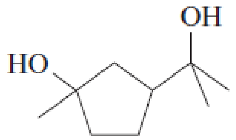
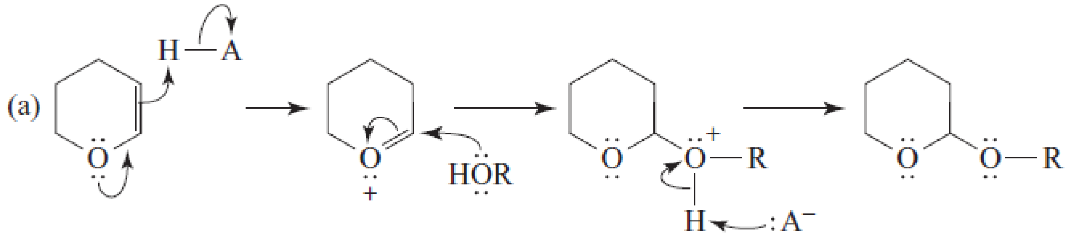


(b) Addition would take place at the ketone group as well as at the ester group. The product (after hydrolysis) would be



15.14



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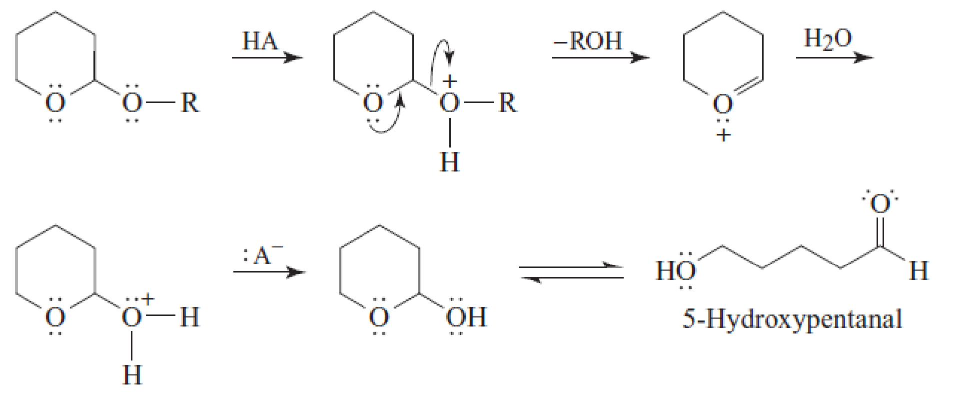
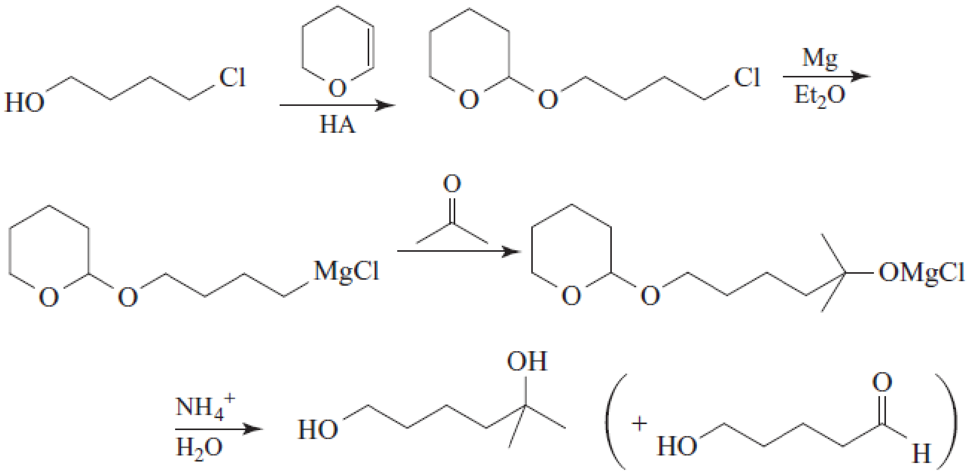
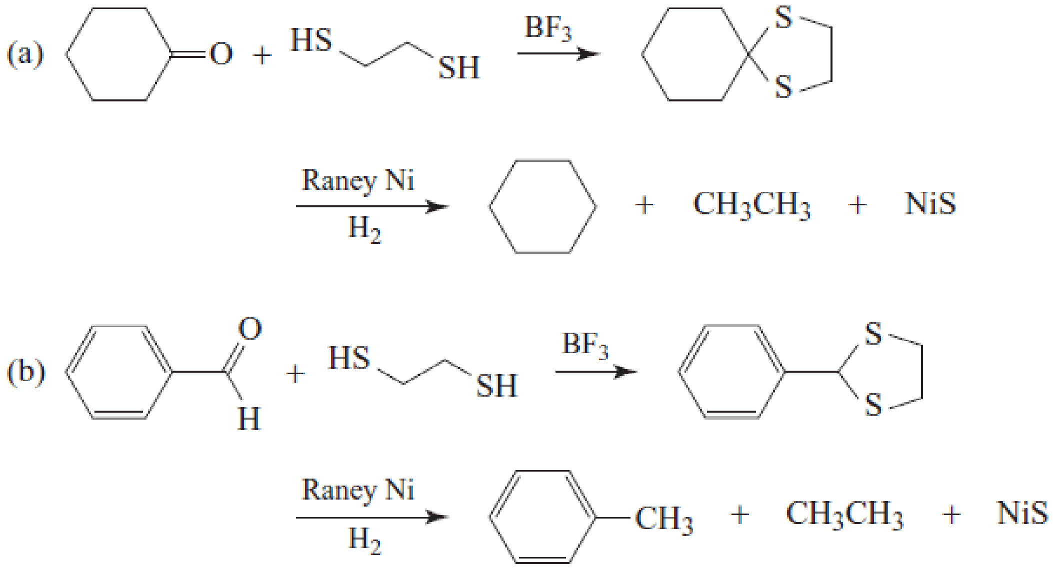
(b) Tetrahydropyranyl ethers are acetals; thus, they are stable in aqueous base and hydrolyze readily in aqueous acid.



(c)



15.15



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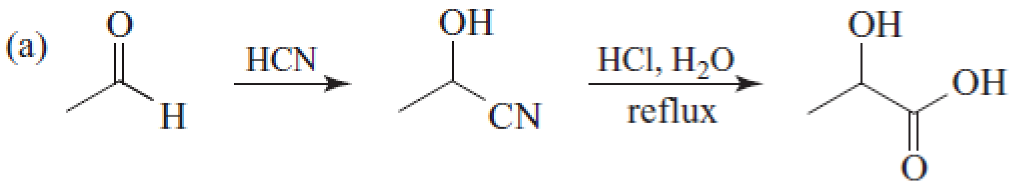
15.16



Lactic acid

(b) A racemic form

15.17

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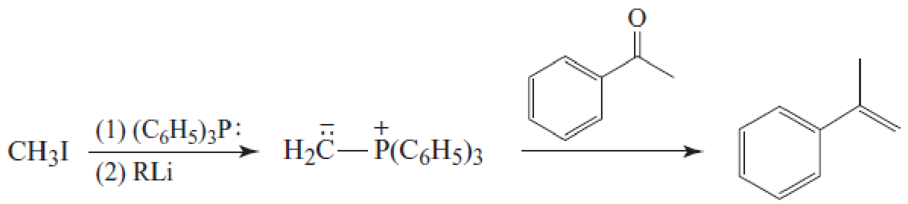
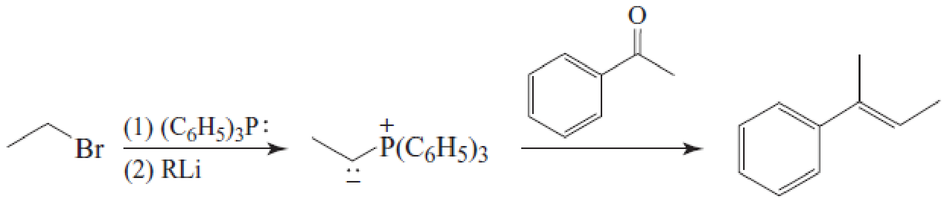
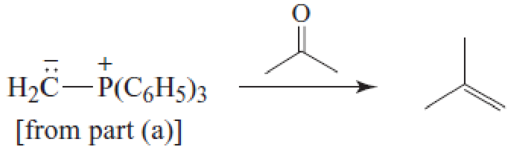
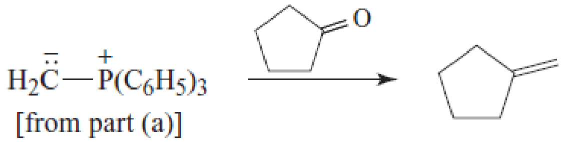
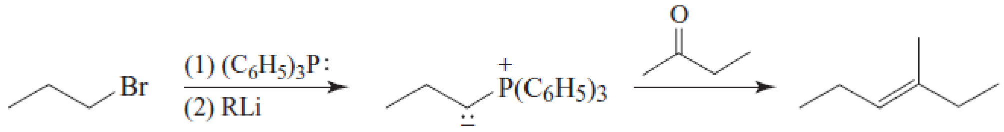
(a) 

(b) 

(c) 

(d) 

(e) 

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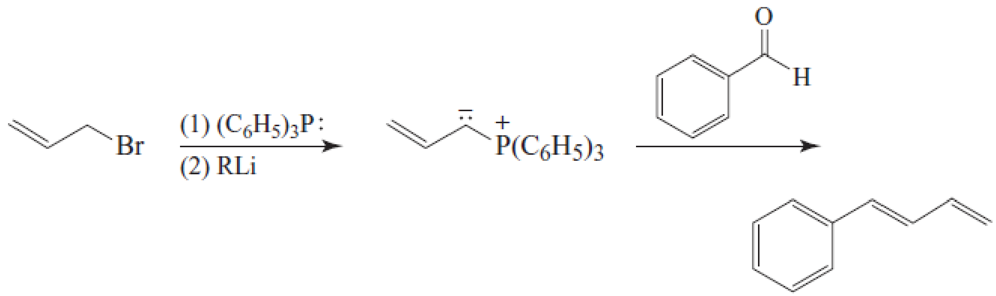
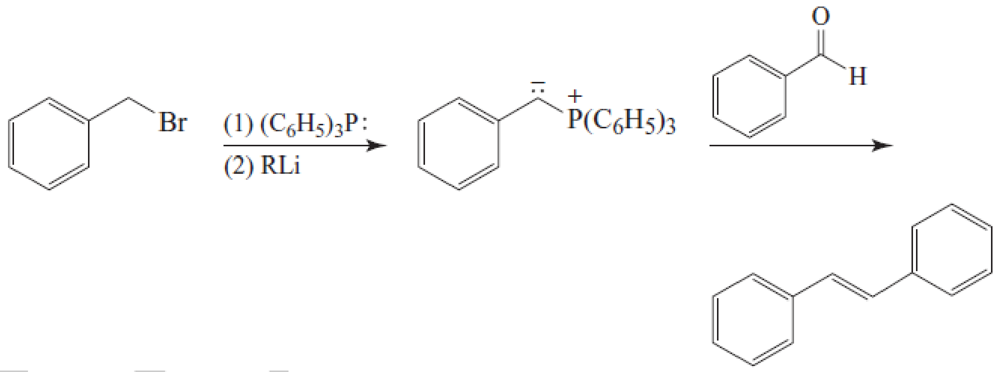
(f) 

(g) 

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15.18

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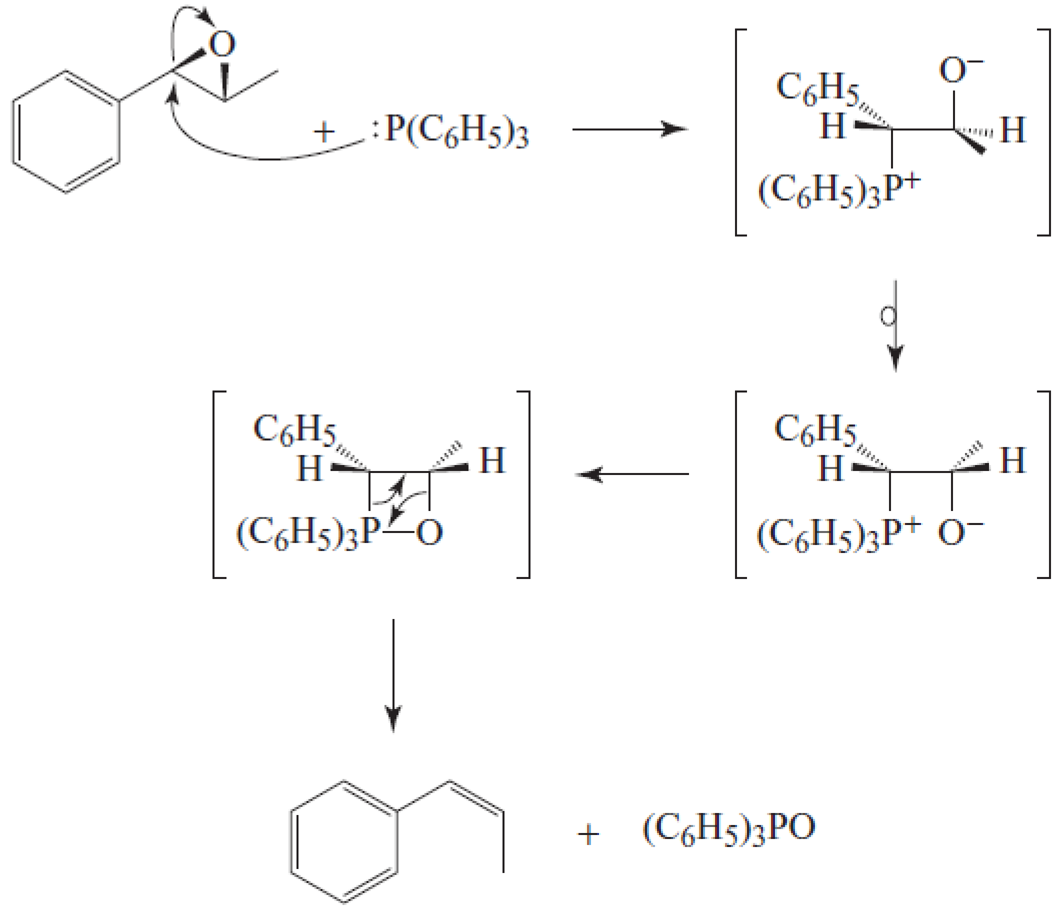
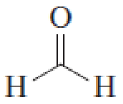
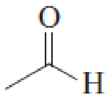


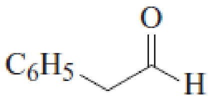
Review Problems

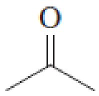
Reactions and Nomenclature

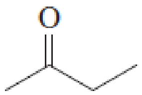
15.19

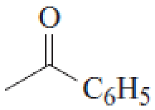
(a)  Methanal

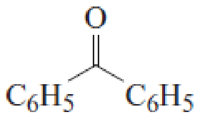
(b)  Ethanal

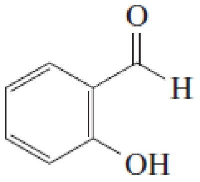
(c)  Phenylethanal

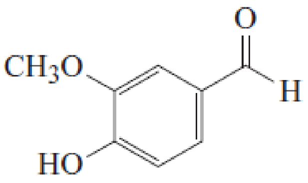
(d)  Propanone

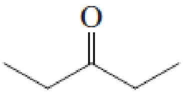
(e)  Butanone

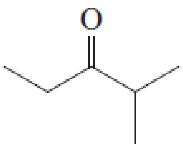
(f)  1-Phenylethanone or methyl phenyl ketone

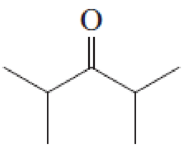
(g)  Diphenylmethanone or diphenyl ketone

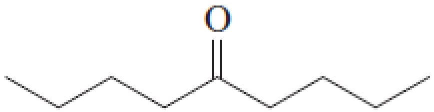
(h)  2-Hydroxybenzaldehyde or *o*-hydroxybenzaldehyde

(i)  4-Hydroxy-3-methoxybenzaldehyde

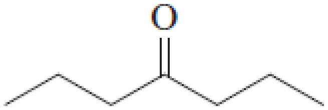
(j)  3-Pentanone

(k)  2-Methyl-3-pentanone

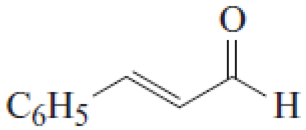
(l)  2,4-Dimethyl-3-pentanone

(m) 

5-Nonanone

(n) 

4-Heptanone

(o) 

(*E*)-3-Phenylpropenal

15.20

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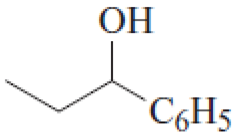
(a)

(b) 

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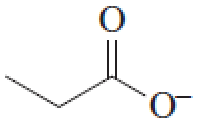
(d) 

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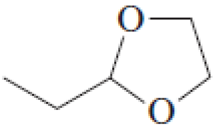
(g) 

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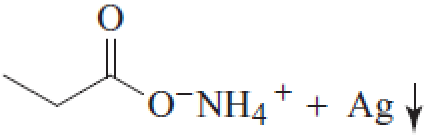
(i) 

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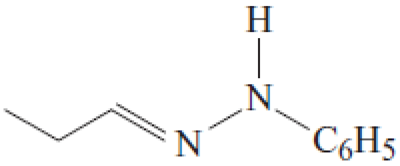
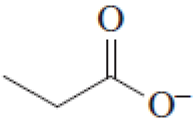
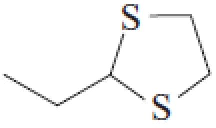
(k) 

(l) 

(m) 

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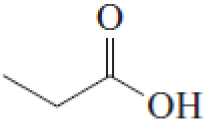
(o) 

15.21

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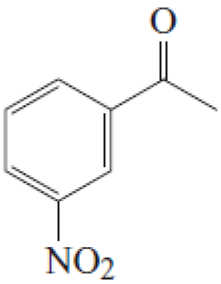
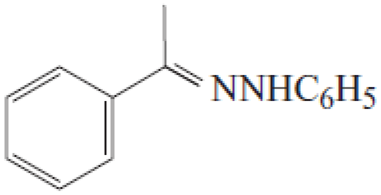
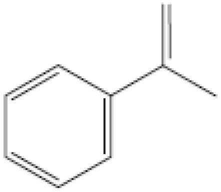
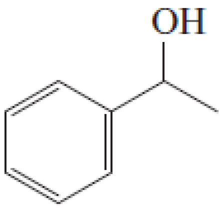
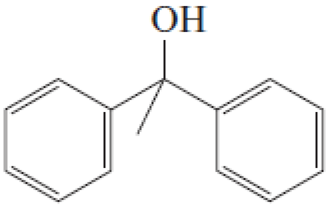
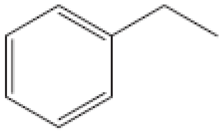
(a) 

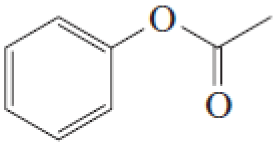
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

15.22

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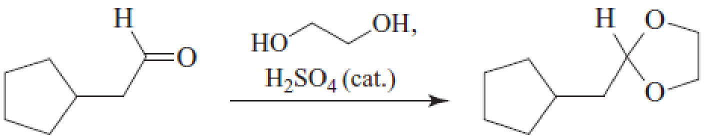
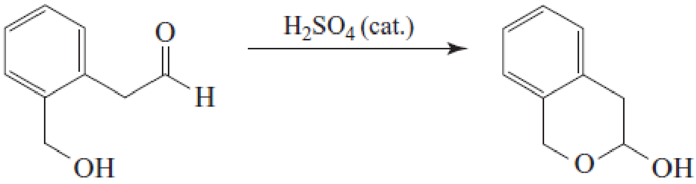
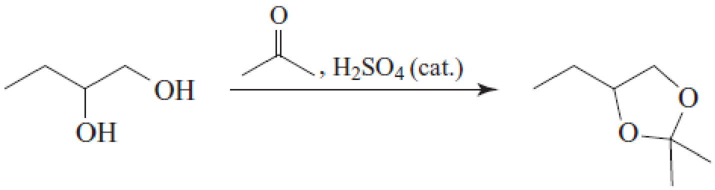
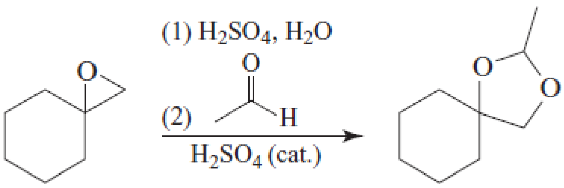
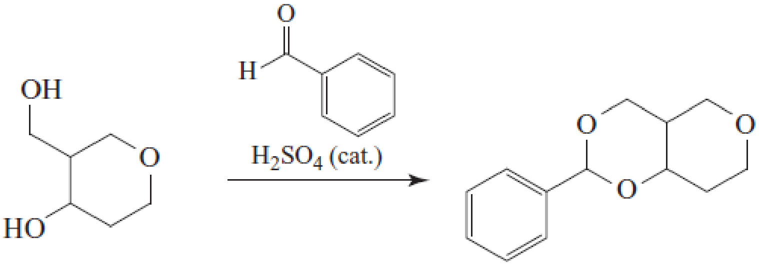
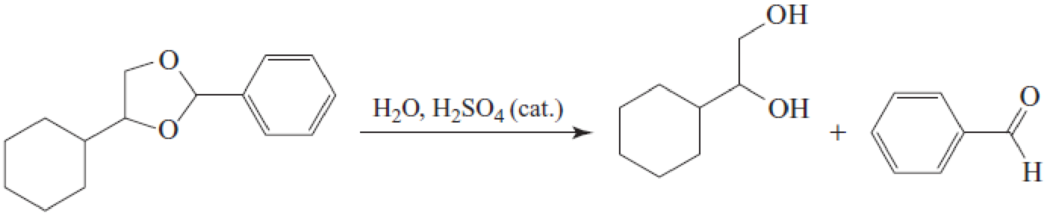
(a) 

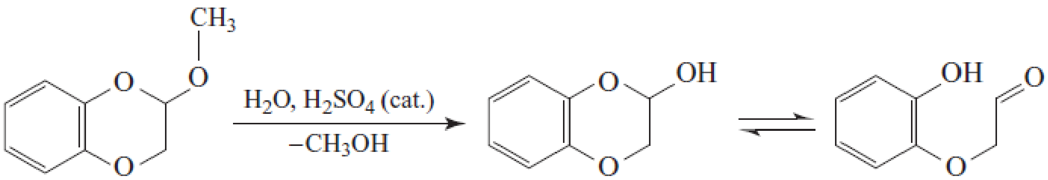
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

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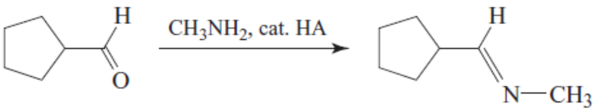
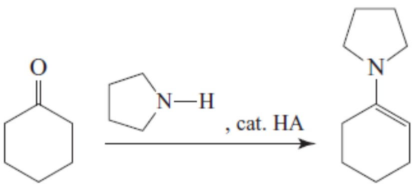
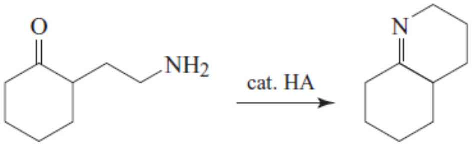
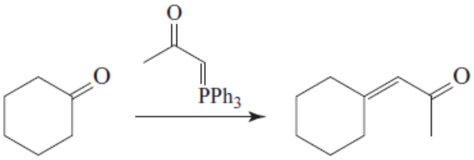
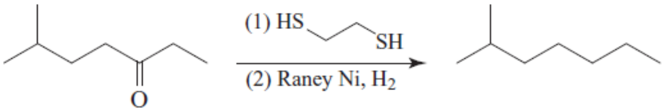
15.23

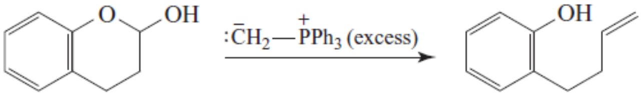
(a) 

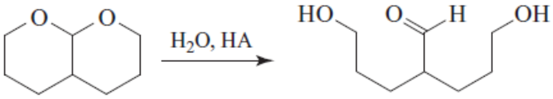
(b) 

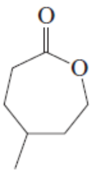
(c) 

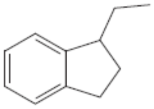
(d) 

(e) 

(f) 

(g) 

(h) 

(i) 

15.24

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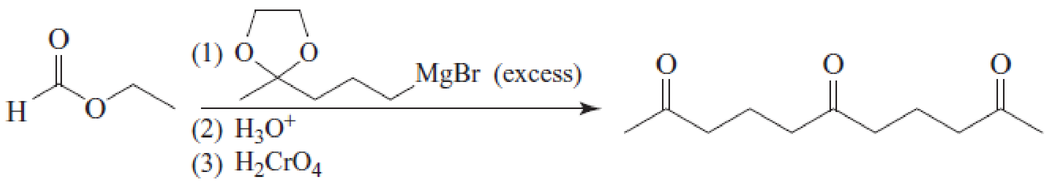
(a)



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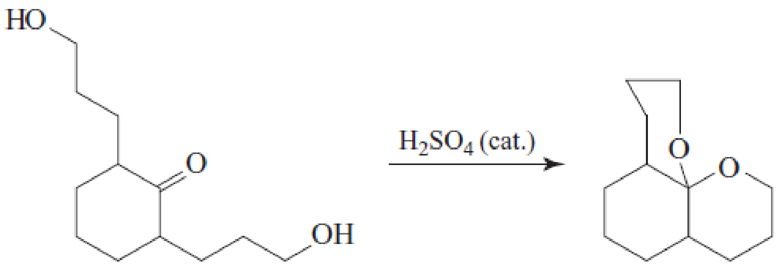

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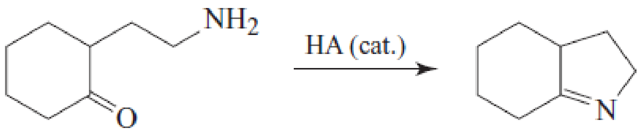

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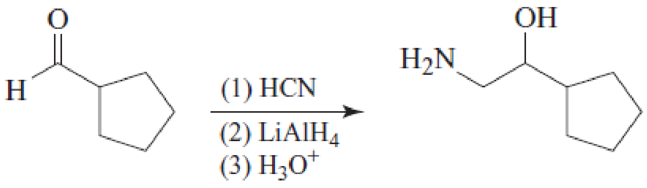

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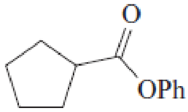

15.25

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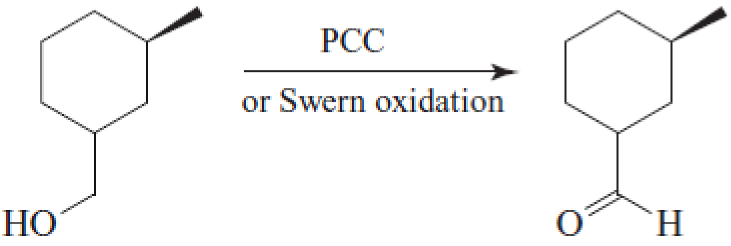
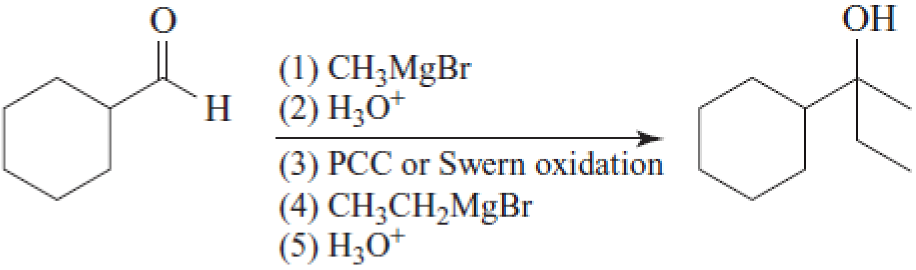
(a) 

(b) 

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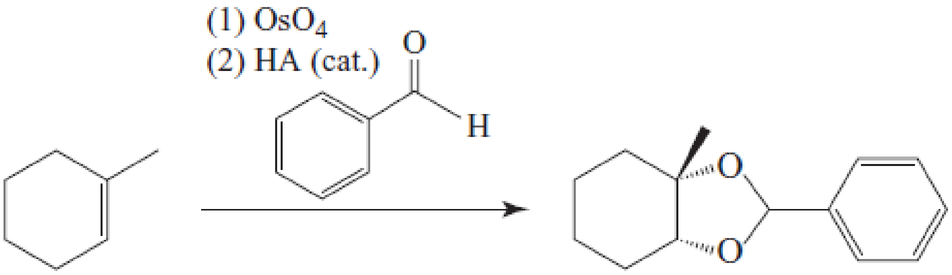
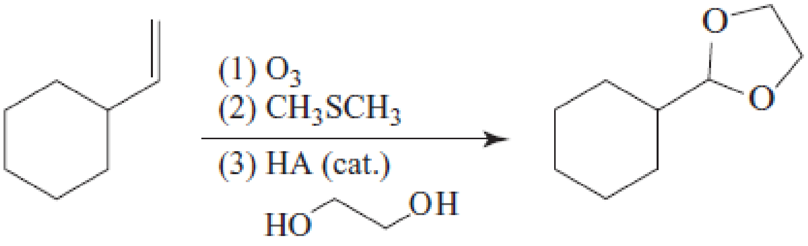
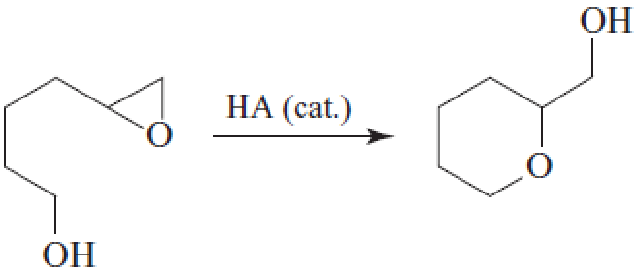
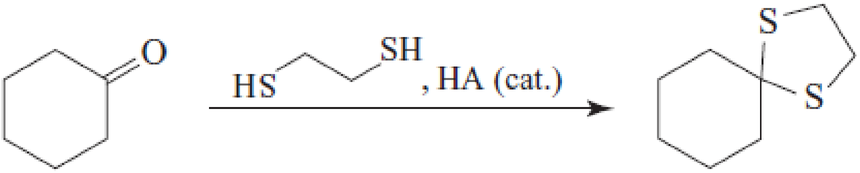
(c) 

(d) 

(e) 

(f) 

(g) $\xrightarrow[\text{heat}]{NH_2NH_2,\ KOH}$

(h) *m*CPBA

15.26

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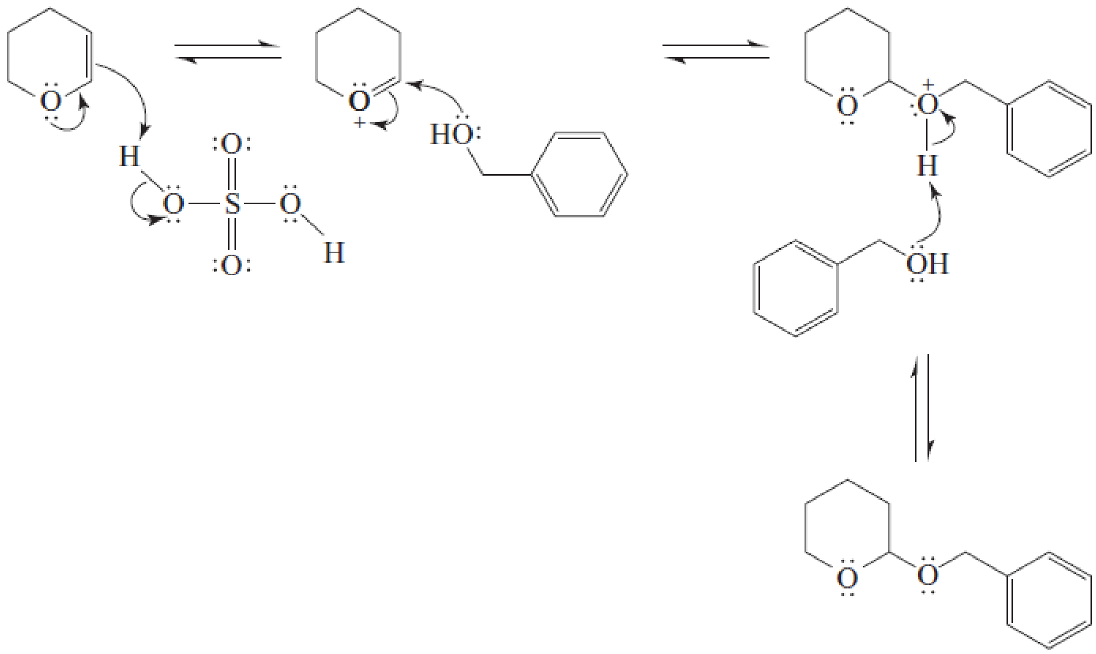
(a)



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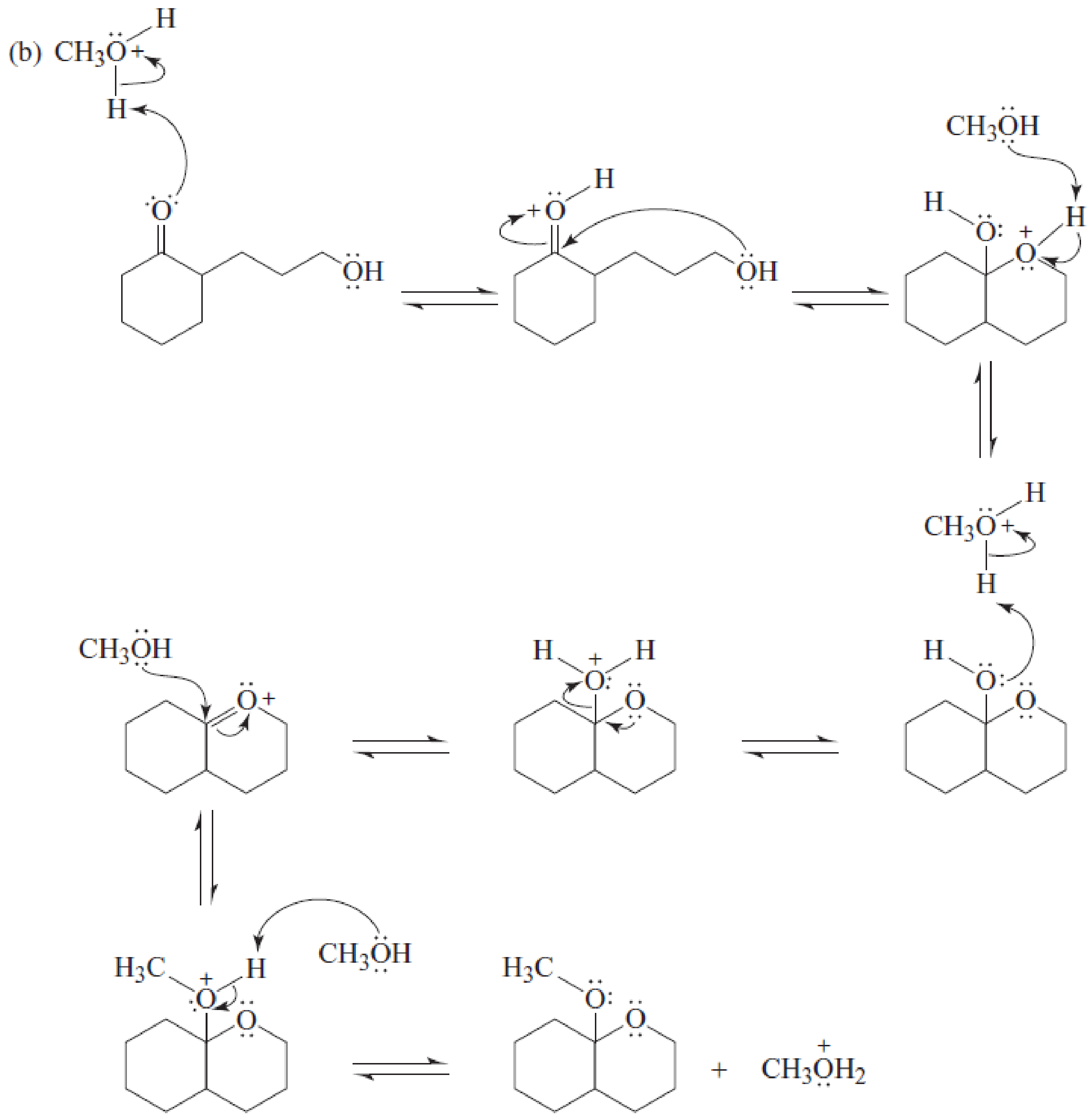
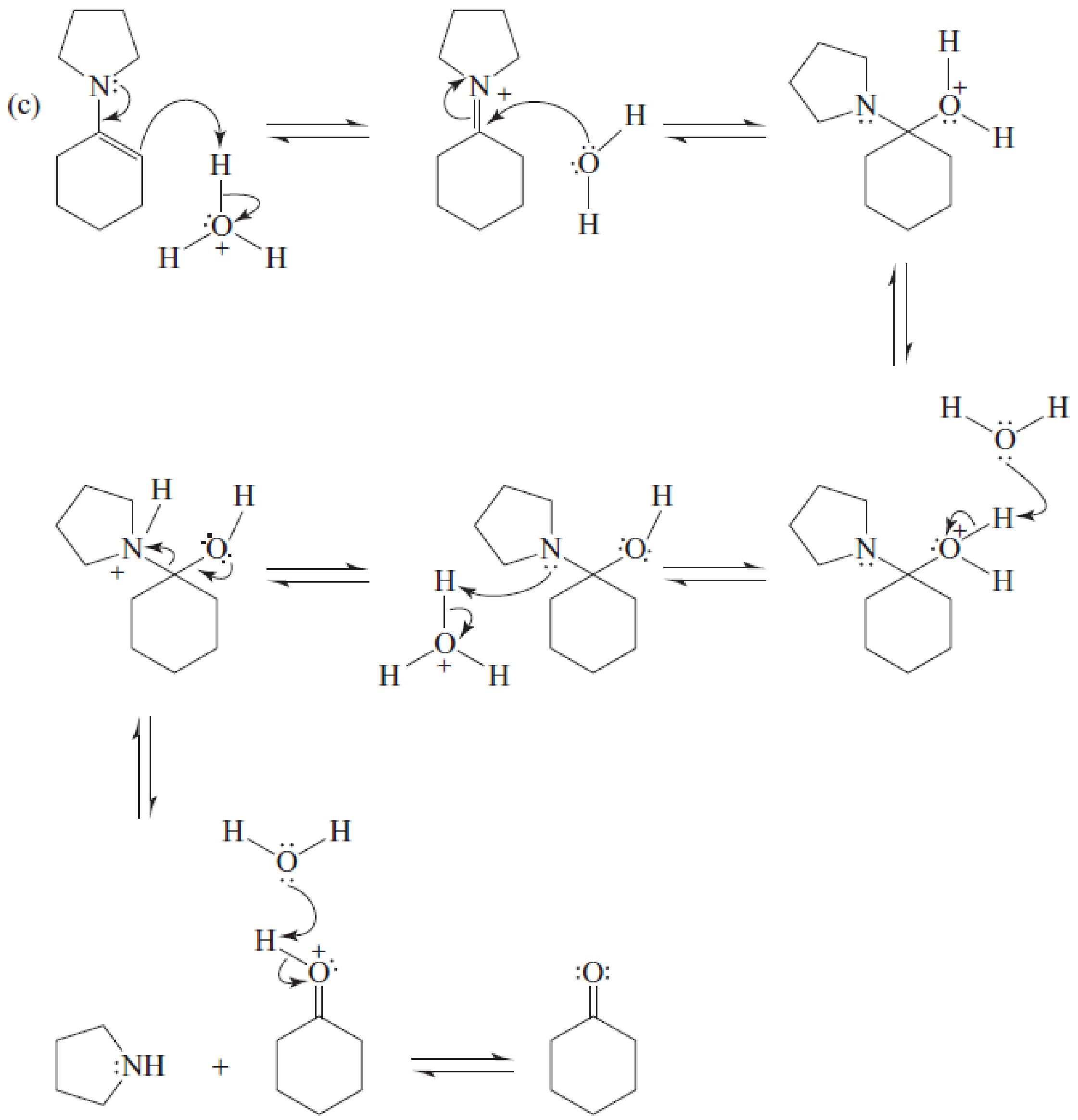

(b)
CH3O+
H
OH
CH3OH
H3C
CH3OH2



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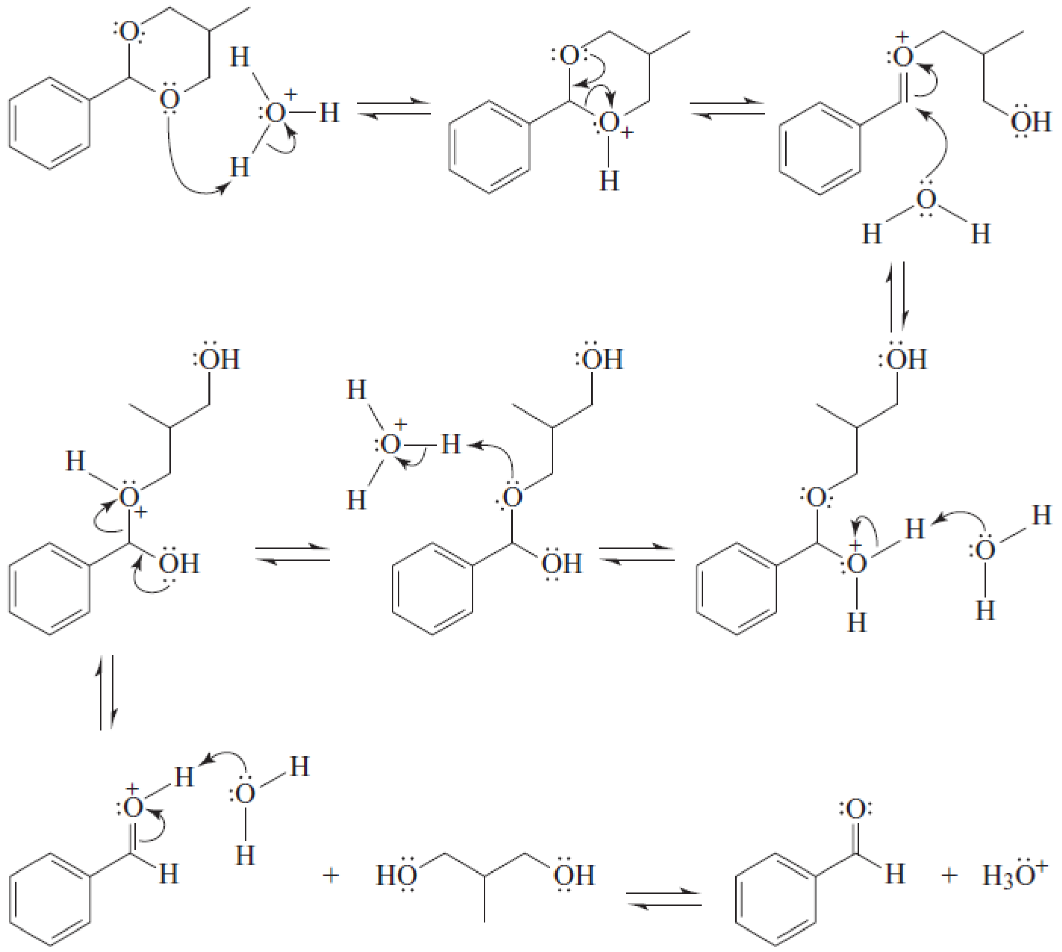
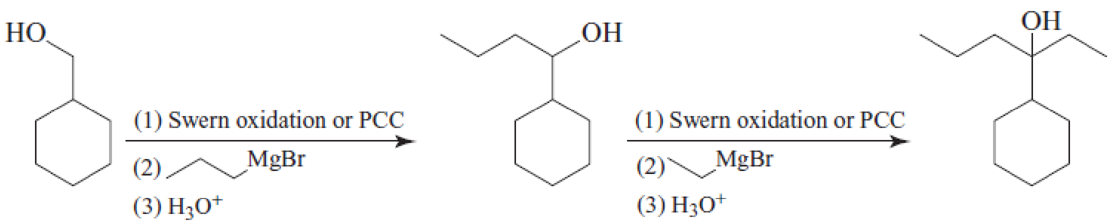
(d)



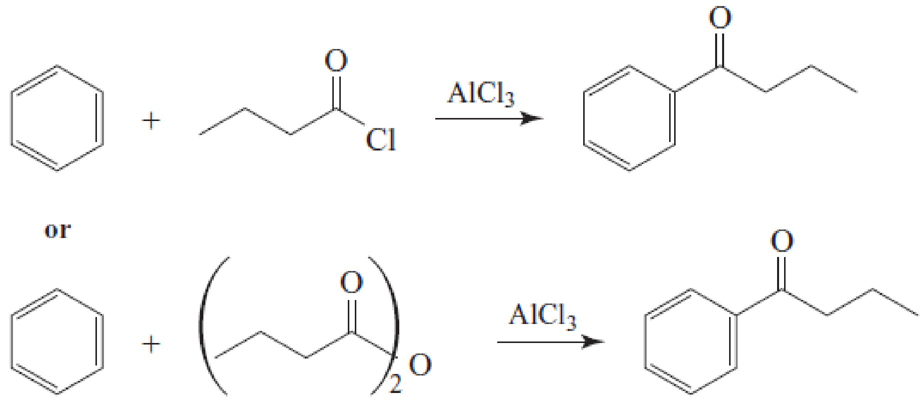
15.27



Synthesis

15.28

(a)



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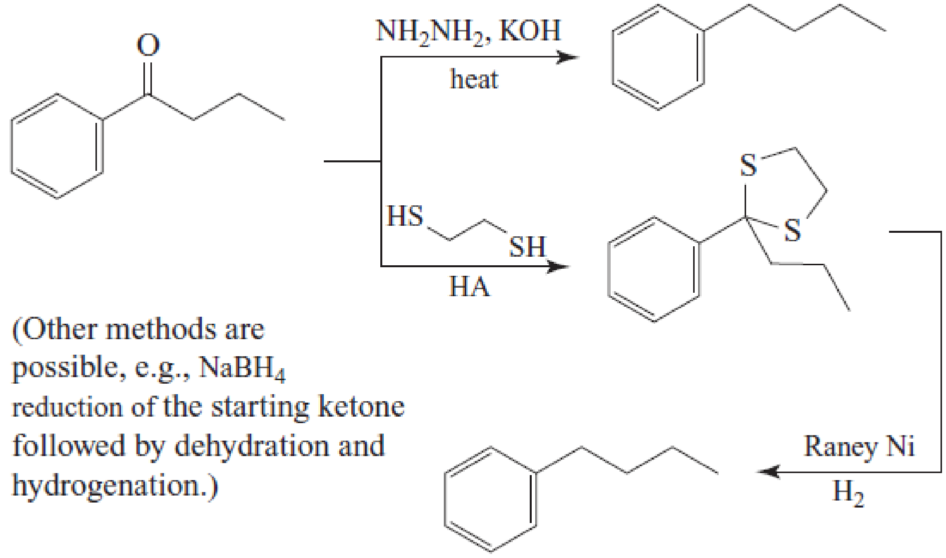

15.29

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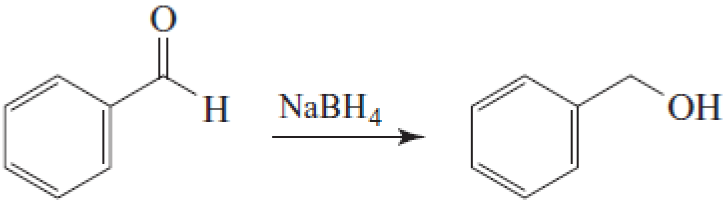
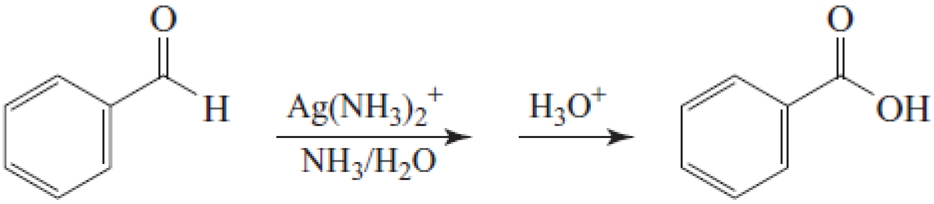
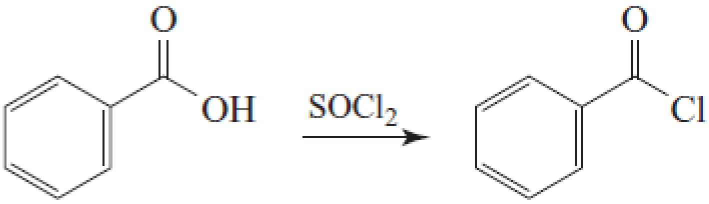
(a) 

(b) 

(c) 

[from (b)]

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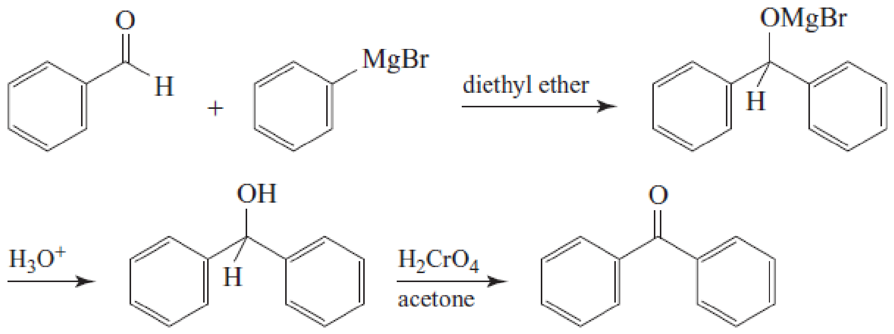
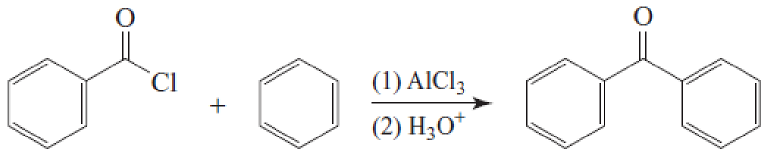
(d) 

or



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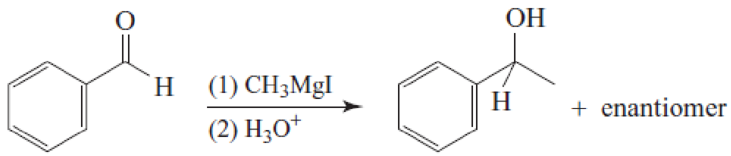
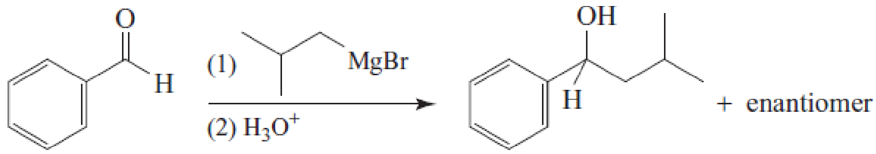
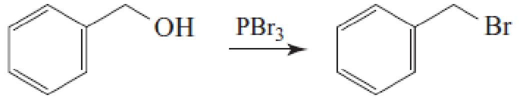
(e) 

(f) 

(g) 

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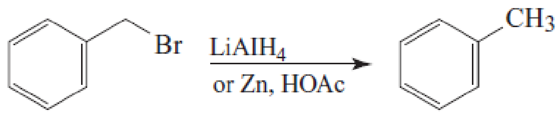
(h) 

[from (g)]

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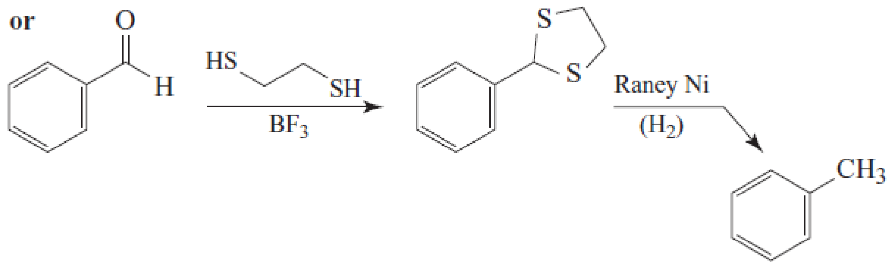
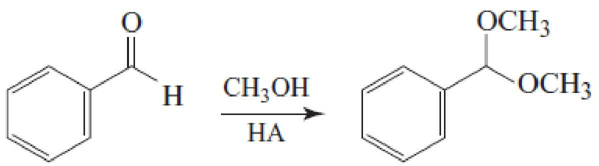
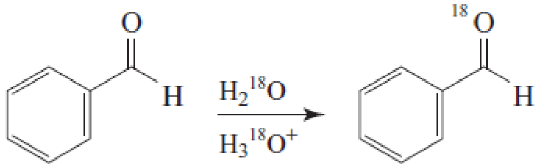


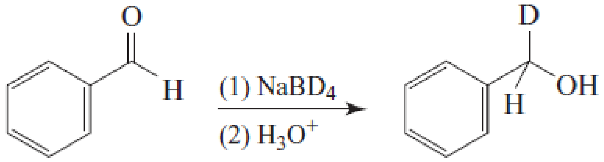
or Wolff-Kishner reduction of benzaldehyde

(Main &

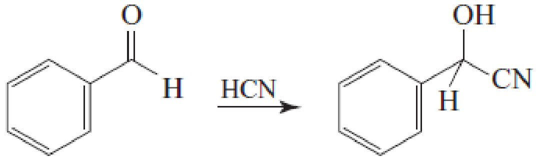
(i) 

(j) 

(See Problem 16.8 for the mechanism)

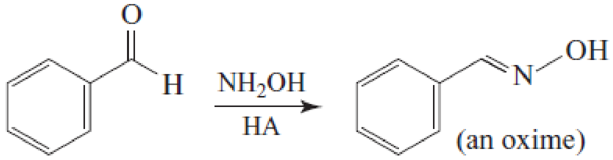
(k) 

+ enantiomer

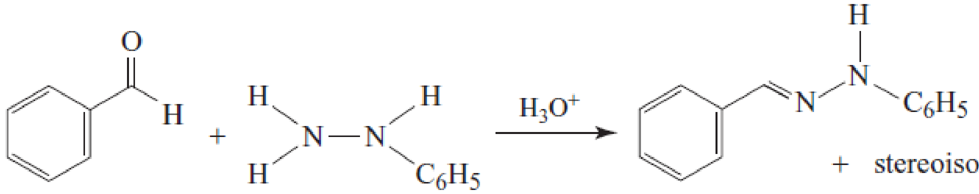
(l) 

+ enantiomer

(a cyanohydrin)

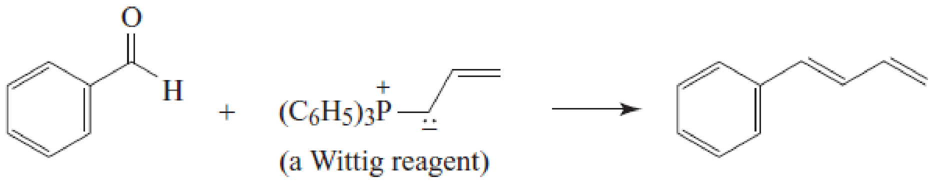
(m) 

+ stereoisomer

(n) 

+ stereoisomer

(a phenylhydrazone)

(o) 

(a Wittig reagent)

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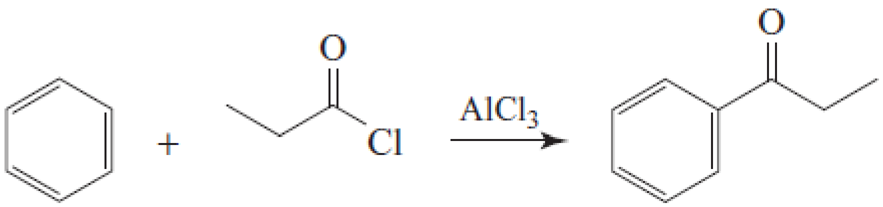
15.30

(a)


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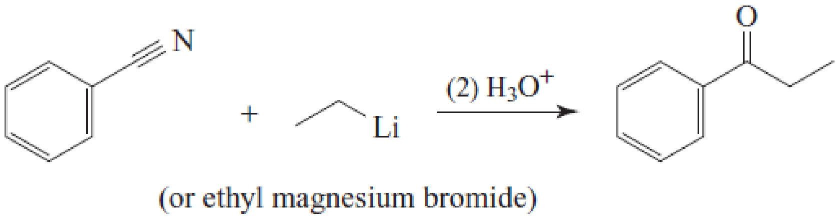
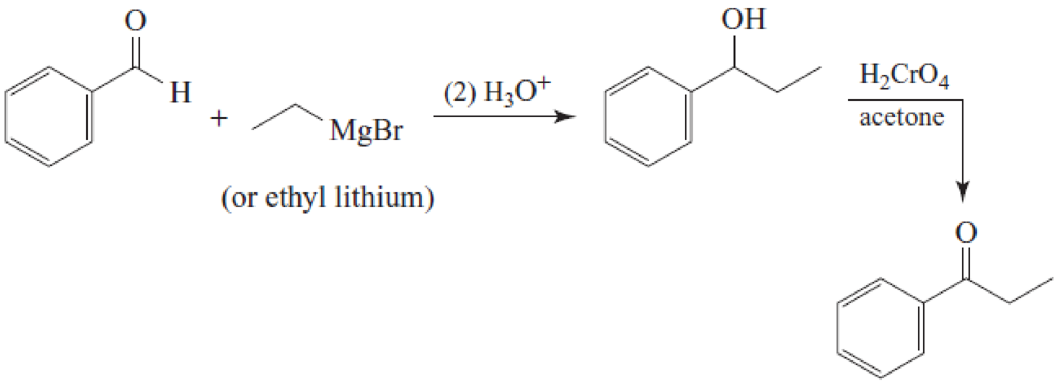


(c)


15.31

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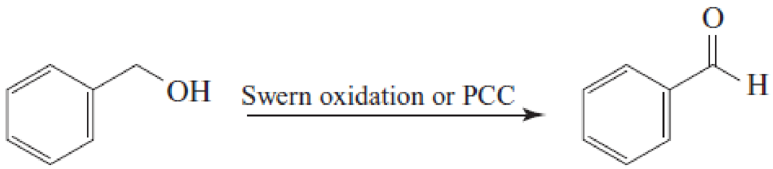
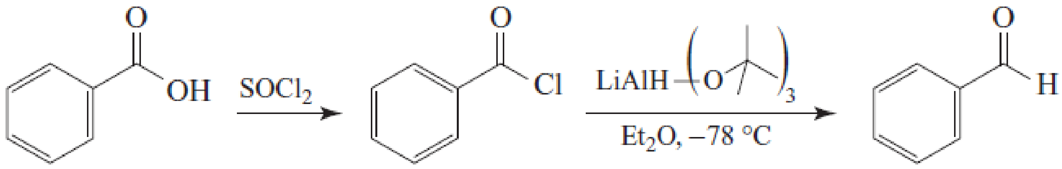
(a)



(b)



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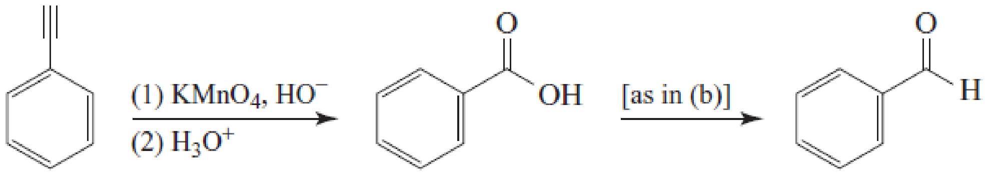
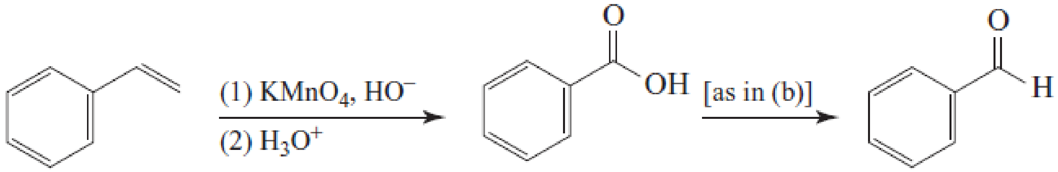
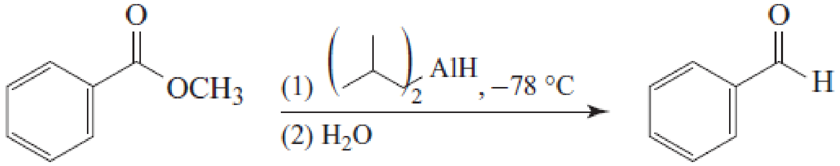


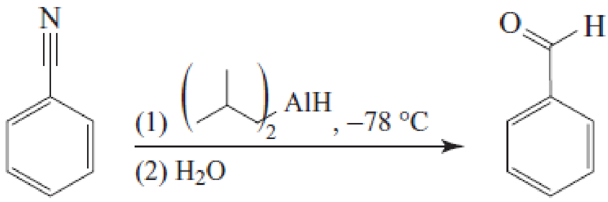
(d)



(e)



(f)



15.32

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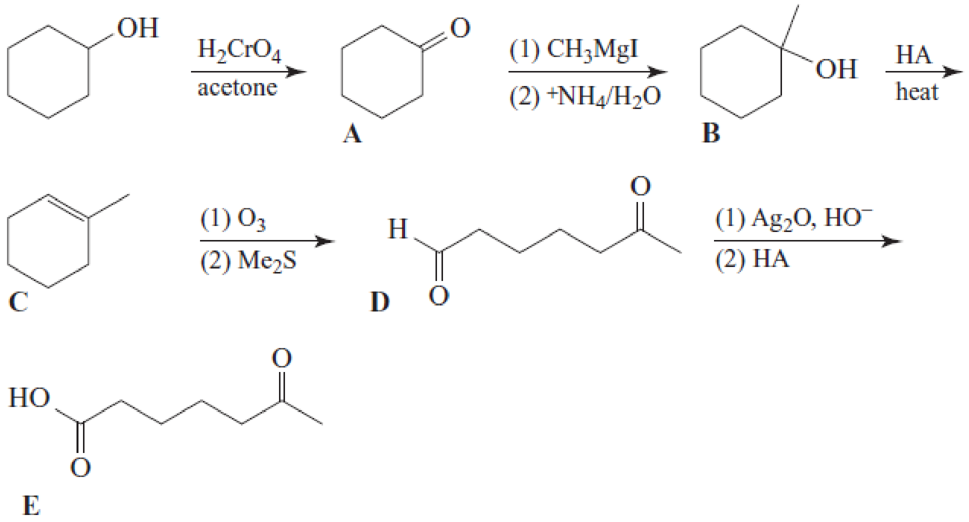
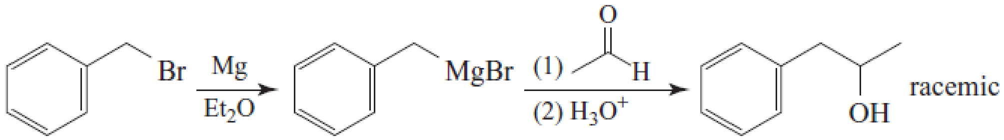
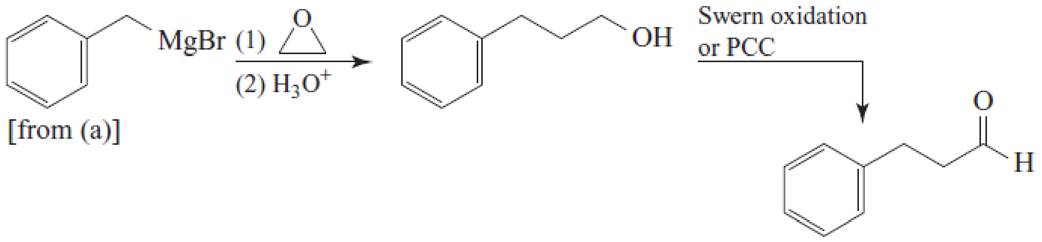


15.33

(a)


(b)


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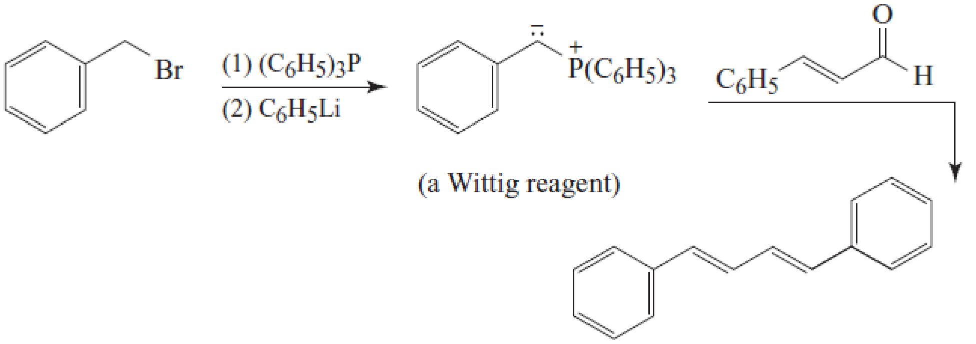

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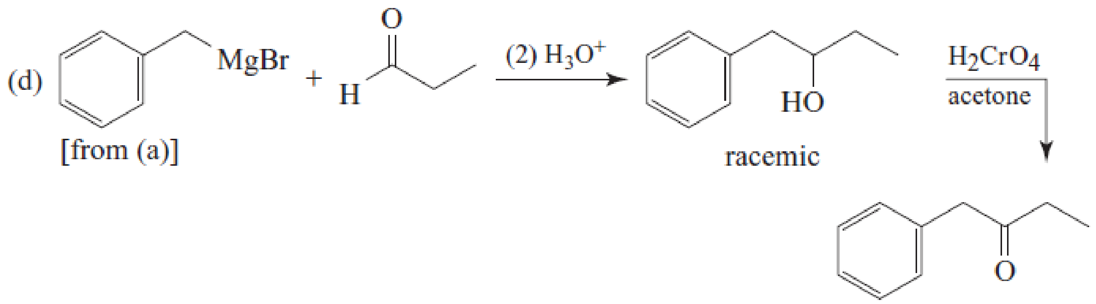
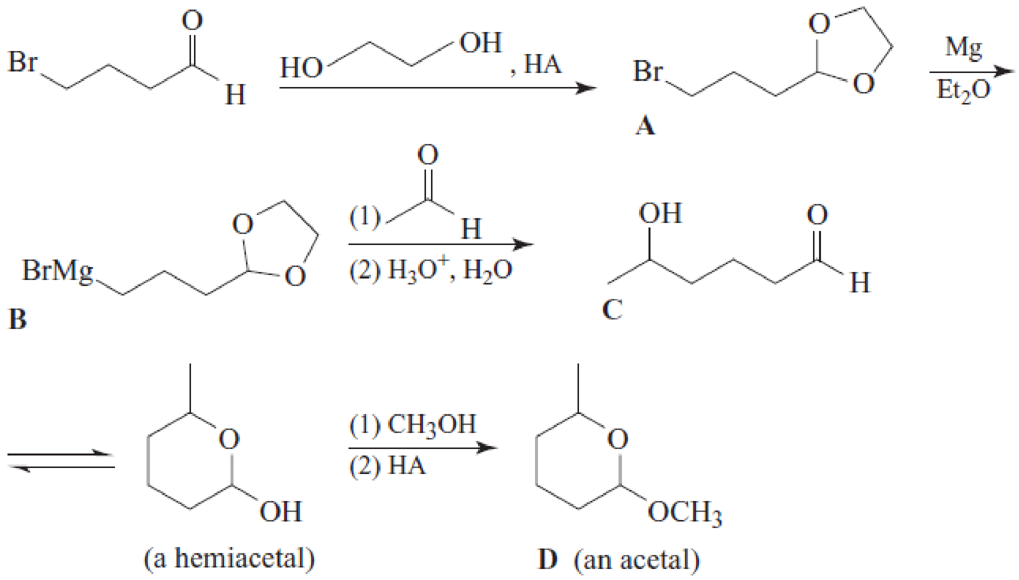
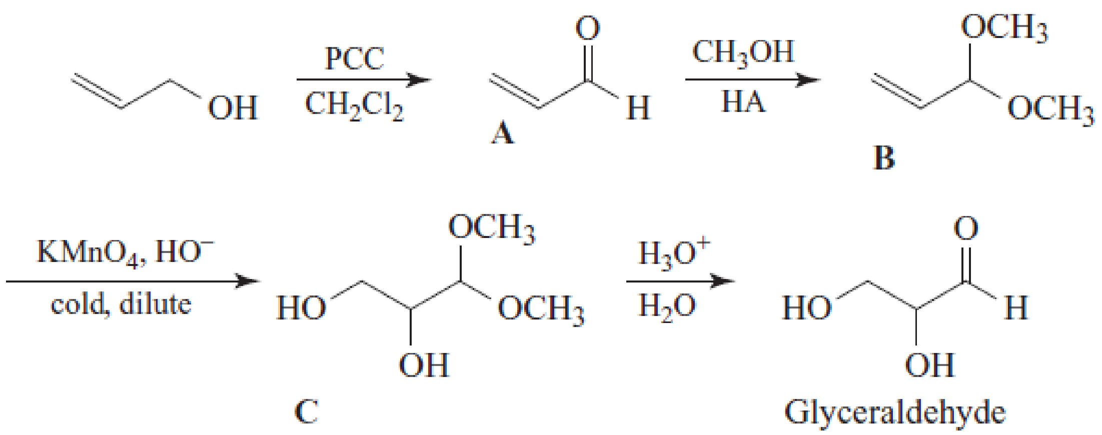

(d)
MgBr
+
H
O
(2) H_3O^+
HO
racemic
[from (a)]
H_2CrO_4
acetone
O

15.34


Br
O
H
HO
OH
, HA
Br
O
O
A
Mg
Et_2O
BrMg
O
O
B
(1)
O
H
(2) H_3O^+, H_2O
OH
O
H
C
O
OH
(a hemiacetal)
(1) CH_3OH
(2) HA
O
OCH_3
D (an acetal)

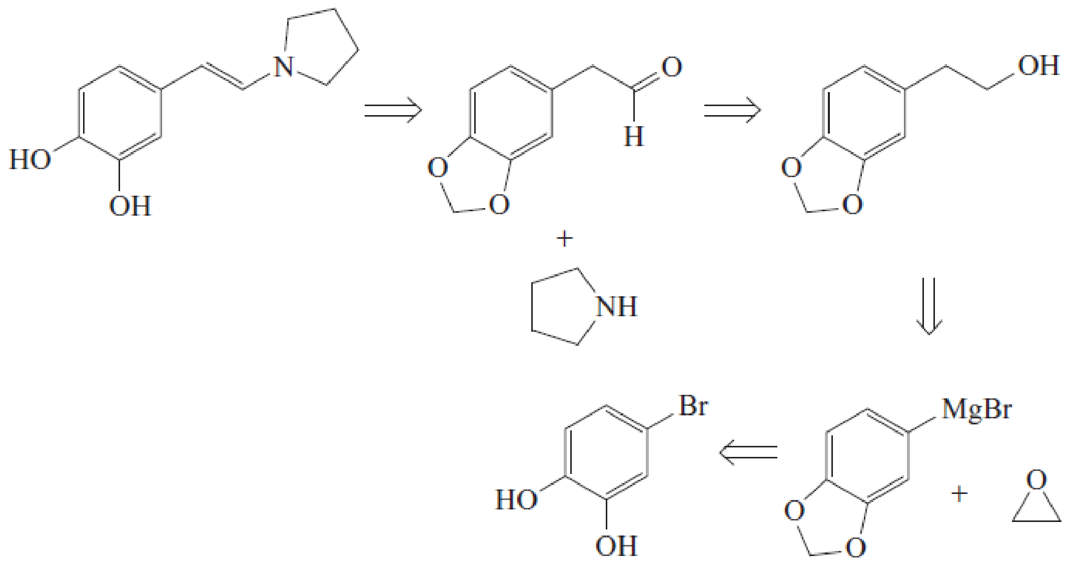
15.35



The product would be racemic since no chiral reagents were used.

15.36

(a) ***Retrosynthetic Analysis***



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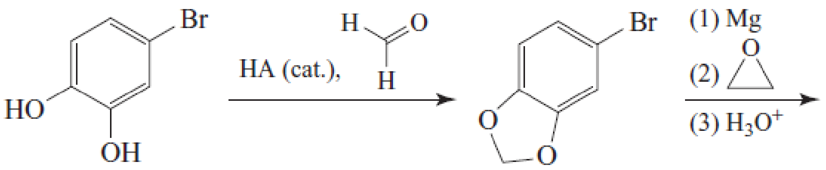
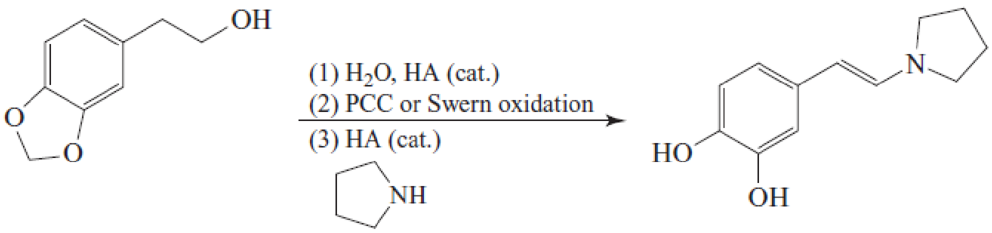
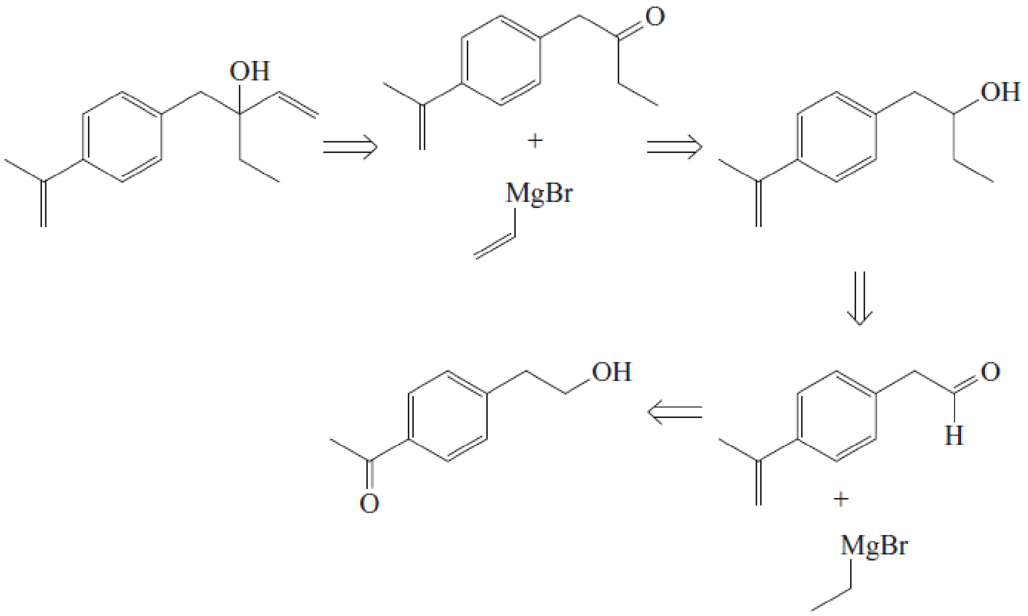
Synthesis





(b) ***Retrosynthetic Analysis***



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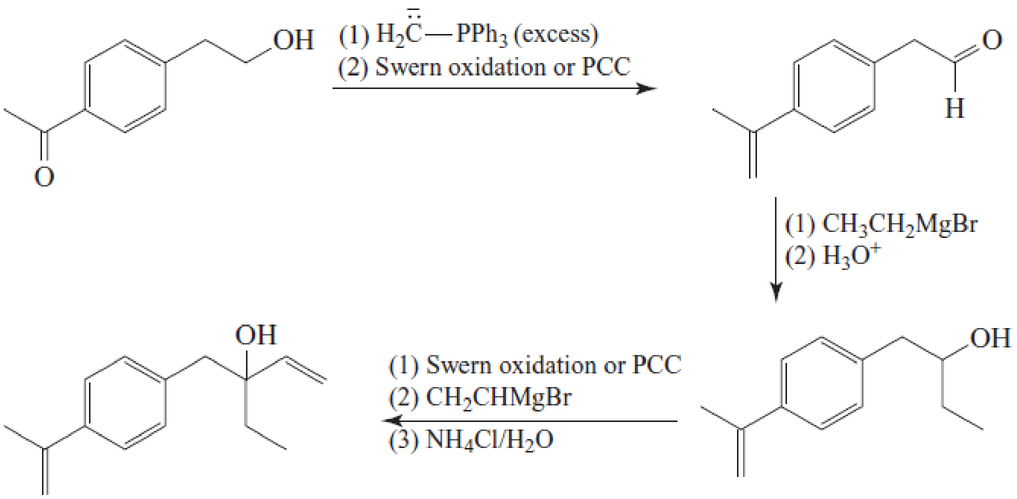
Synthesis



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<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (b) Cl is substituted by H.
2. **(d)** It is Cannizaro reaction and one aldehyde will be oxidized while another one reduced.
3. **(c)** In iii, the product is alcohol.
4. **(c)**
5. **(d)** Both reduction would yield the product.
6. **(b)** The RDS step is the transfer of hydride to the carbonyl group.
7. (**b)** More the electron deficiency on carbonyl C, more is the rate of reaction.
8. **(d)** More the electron density, more is the hydride donation tendency.
9. **(a)**
10. **(a)** It is Cannizaro reaction.
11. **(d)** Less the e^- deficiency on carbonyl C, less is the rate of reaction.
12. **(a)** Compound B is aldehyde as it gives Tollens test while compound A is primary alcohol. Product C is formed by addition followed by dehydration.
13. **(b)** Addition of cyanide occurs more readily on aldehyde as compared to ketone, hence its equilibrium constant for the reverse reaction is lower.
14. **(c)** It is Cannizzaro reaction.
15. **(c)** Fehling is weak oxidizing agent, it only oxidizes aldehyde but not aromatic

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aldehyde.
16. (b) It is nucleophilic addition of cyanide to carbonyl.
17. **(c)** LDA is bulkier base, it will remove the less hindered proton from the left c of the carbonyl C, where methyl group will then be added. While in B, methyl will be added to the right C of carbonyl.
18. **(d)** Ether does not give reaction with 2,4-DNP and active metal.
19. **(c)** Cannizzaro followed by dehydration.
20. **(a)** More the electron deficiency, more is the rate of reaction.
21. (b)
22. **(d)**
23. **(d)**
24. (d)
25. (d)
26. **(d)**
27. **(d)**
28. **(b)**

<H2> Linked Comprehension Type

1. (c)
2. **(b)**
3. **(b)**
<H2> Matrix Match Type

1. a→(p, q, s); b→(p); c→(p, q, s); d→(p, q, s)

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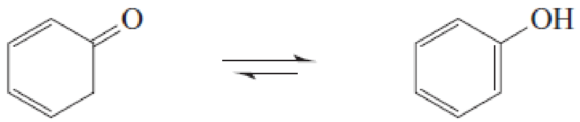
Chapter 16: Aldehyde and Ketones II. Aldol Reactions

Practice Problems

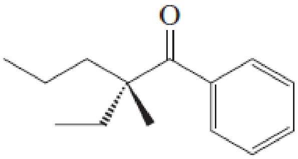
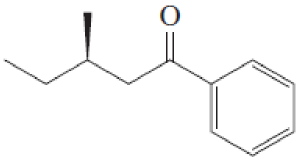
16.1



Cyclohexa-2,4-dien-1-one (keto form) — Phenol (enol form)

The enol form is aromatic, and it is therefore stabilized by the resonance energy of the benzene ring.

16.2

No.  does not have a hydrogen attached to its α-carbon atom (which is a chirality center) and thus enol formation involving the chirality center is not possible. With  the chirality center is a β carbon and thus enol formation does not affect it.

16.3

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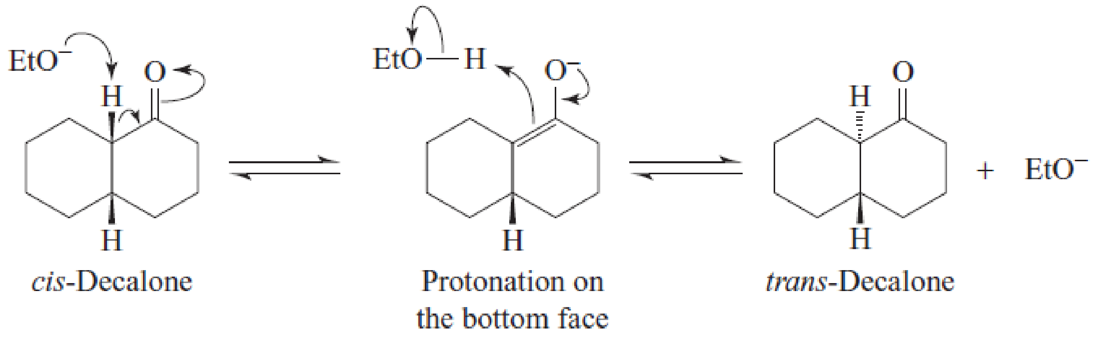

16.4

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The reaction is said to be "base promoted" because base is consumed as the reaction takes place. A catalyst is, by definition, not consumed.

16.5

(a) The slow step in base-catalyzed racemization is the same as that in base-promoted halogenation—*the formation of an enolate anion.* (Formation of an enolate anion from 2-methyl-1-phenylbutan-1-one leads to racemization because the enolate anion is achiral. When it accepts a proton, it yields a racemic form.) The slow step in acid-catalyzed racemization is also the same as that in acid-catalyzed halogenation—*the formation of an enol.* (The enol, like the enolate anion, is achiral and tautomerizes to yield a racemic form of the ketone.)

(b) According to the mechanism given, the slow step for acid-catalyzed iodination (formation of the enol) is the same as that for acid-catalyzed bromination. Thus, we would expect both reactions to occur at the same rate.

(c) Again, the slow step for both reactions (formation of the enolate anion) is the same, and consequently, both reactions take place at the same rate.

16.6

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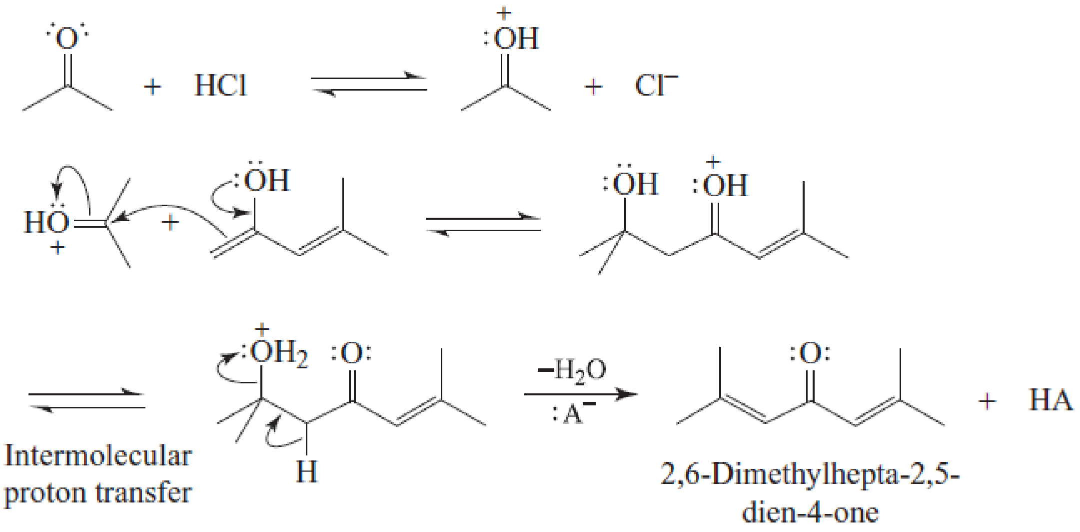
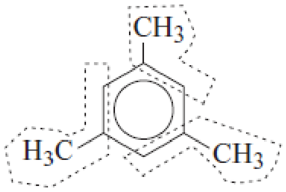


16.7

Drawing the molecules as they will appear in the final product helps to visualize the necessary steps:



Mesitylene

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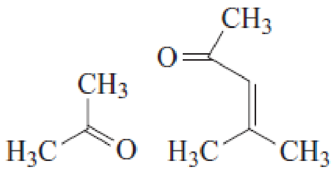
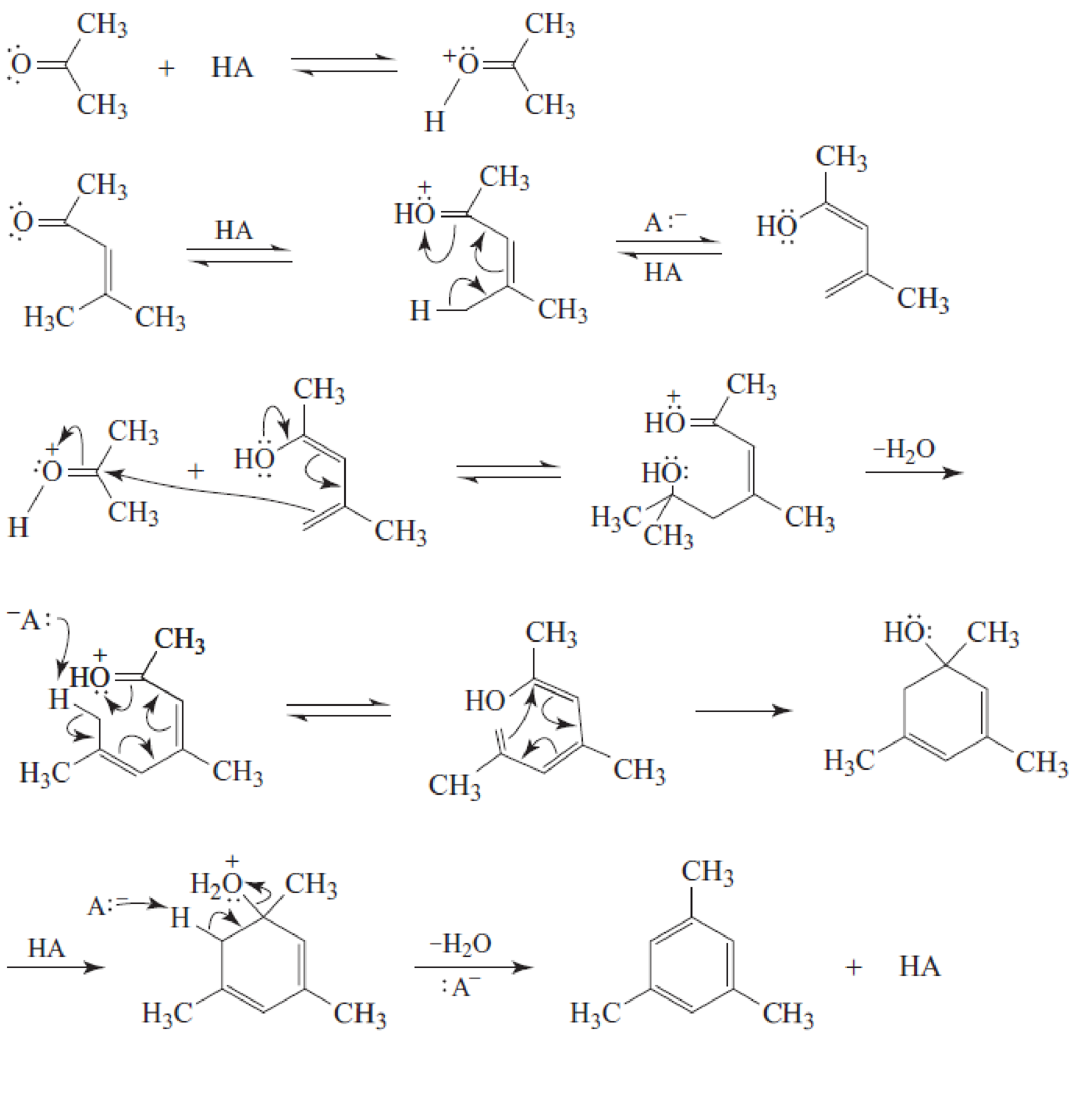
The two molecules that lead to mesitylene are shown as follows:

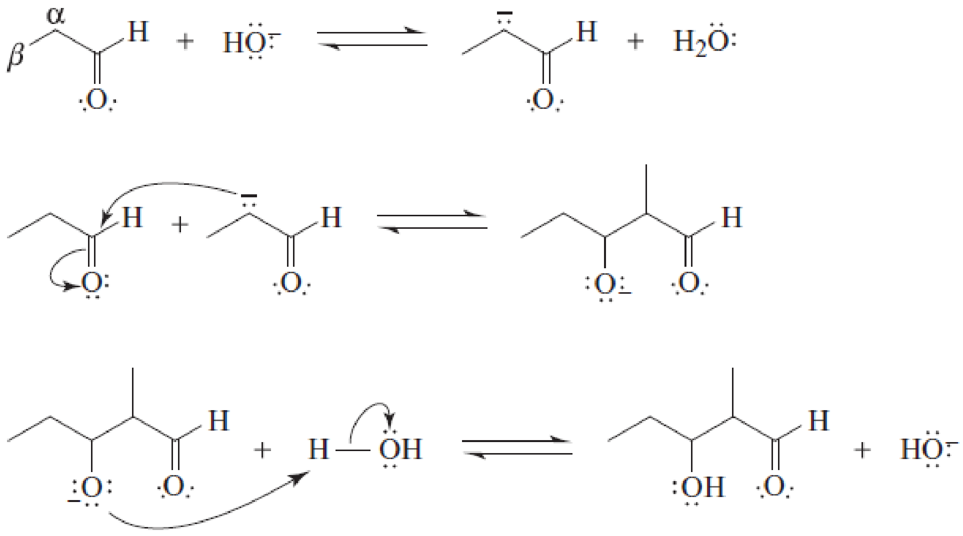


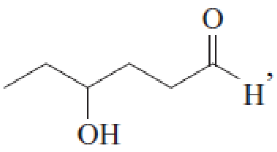
(4-Methylpent-3-en-2-one is formed by an acid-catalyzed condensation between two molecules of acetone as shown in the text.)

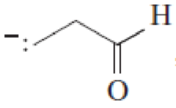
The mechanism is the following.

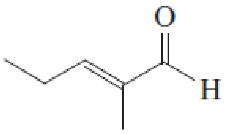


16.8

(a) 

(b) To form , a hydroxide ion would have to remove a β proton in the first step. This does not happen because the anion that would be produced,

, cannot be stabilized by resonance.

(c) 

[both (*E*) and (*Z*)]

16.9

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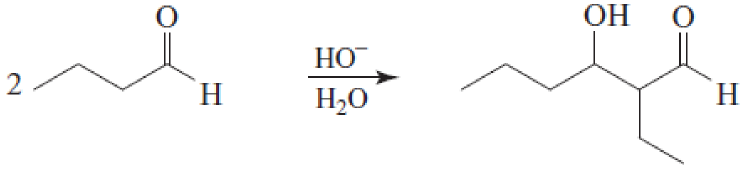
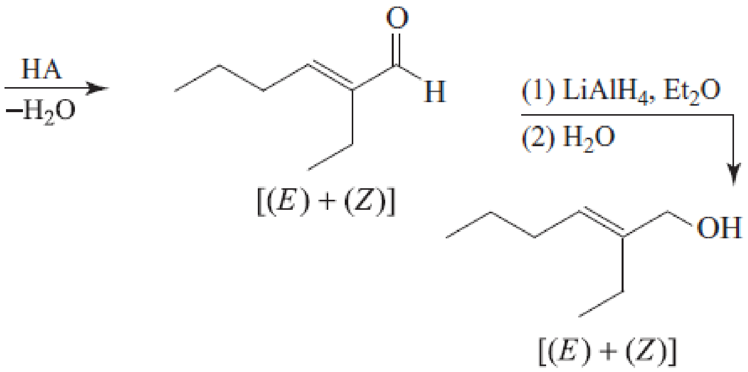
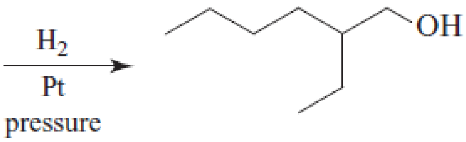
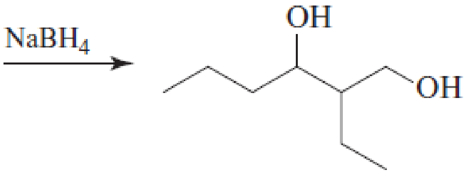
(a) 

(b) Product of (a) 

(c) Product of (b) 

(d) Product of (a) 

16.10

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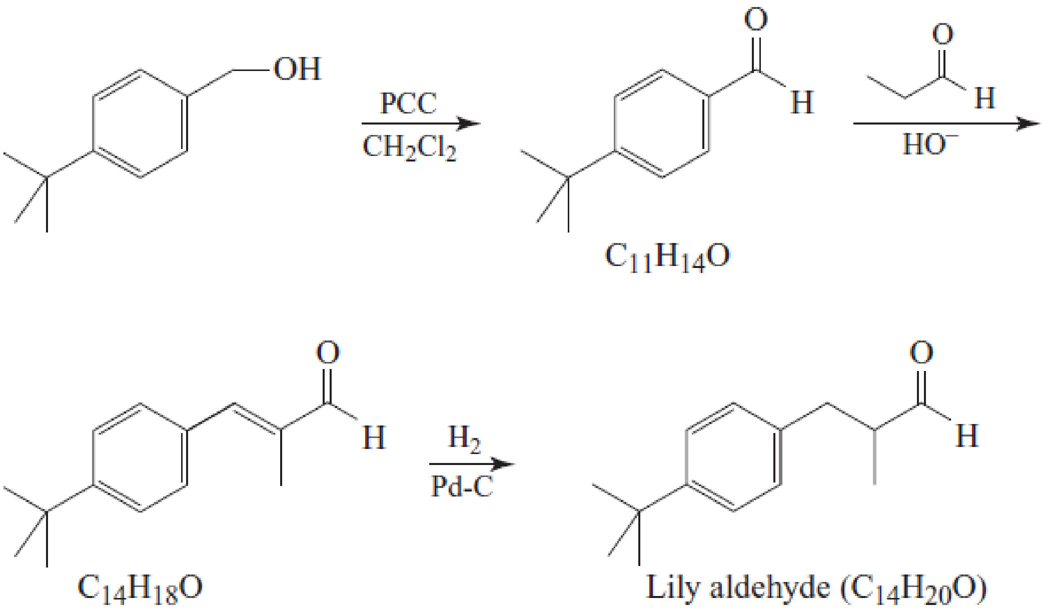
OH
PCC
CH2Cl2
O
H
C11H14O
O
H
HO−
O
H
C14H18O
H2
Pd-C
O
H
Lily aldehyde (C14H20O)

16.11

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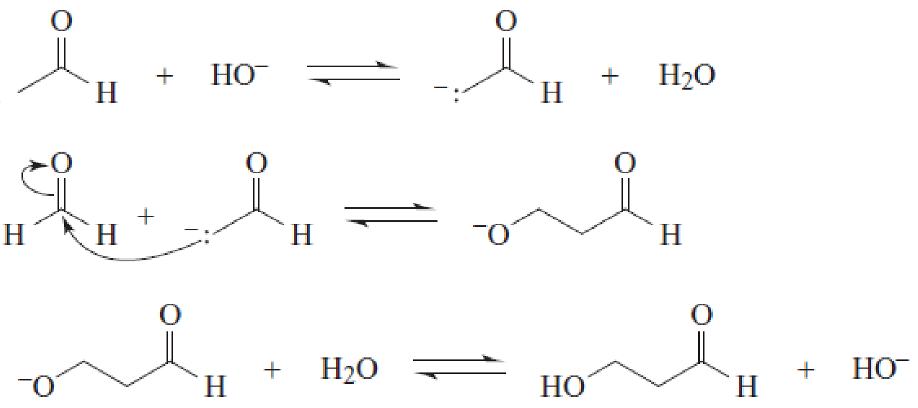
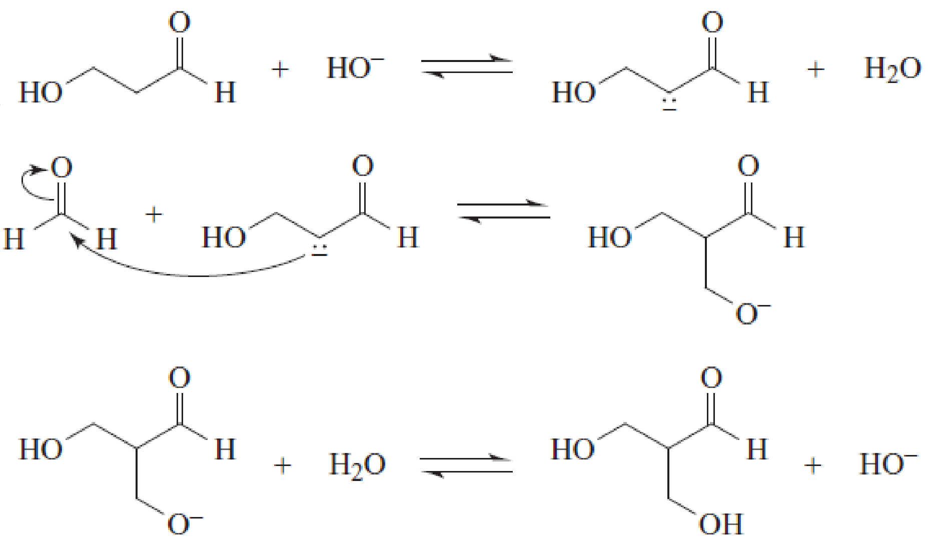
Three successive aldol additions occur.

First Aldol Addition



Second Aldol Addition



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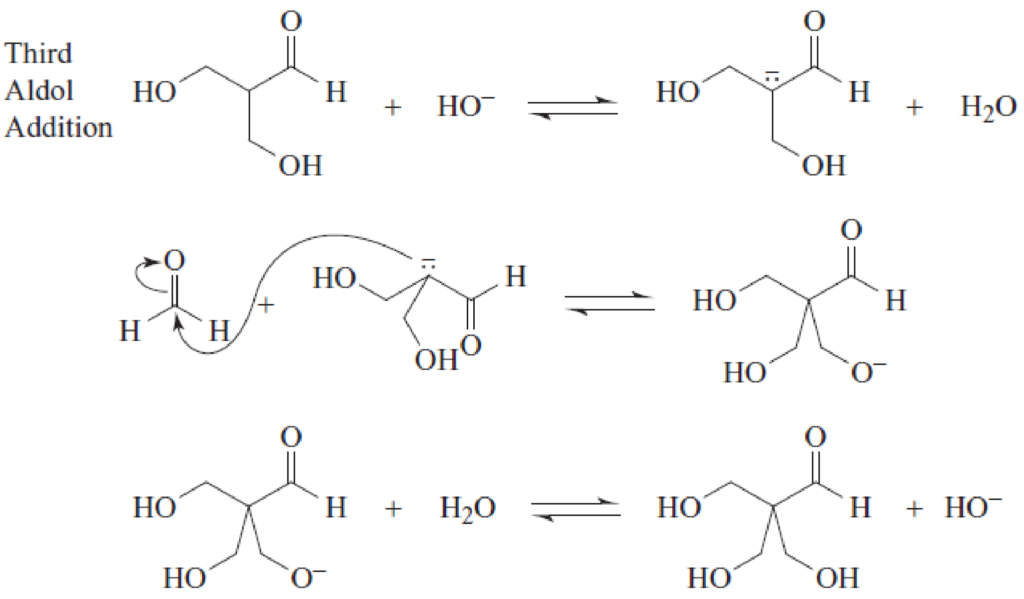
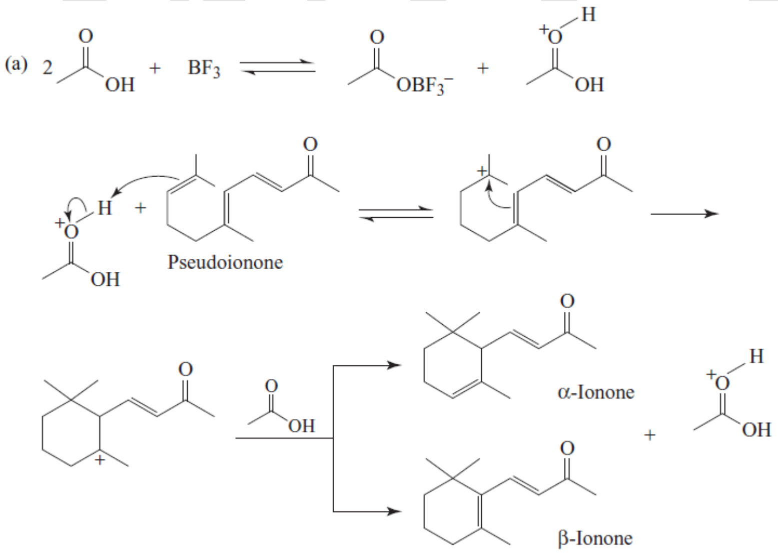


16.12



(b) In β-ionone both double bonds and the carbonyl group are conjugated; thus it is more stable.

(c) β-Ionone, because it is a fully conjugated unsaturated system.

16.15

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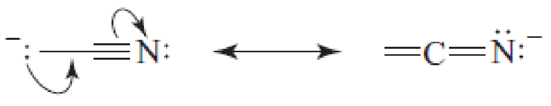
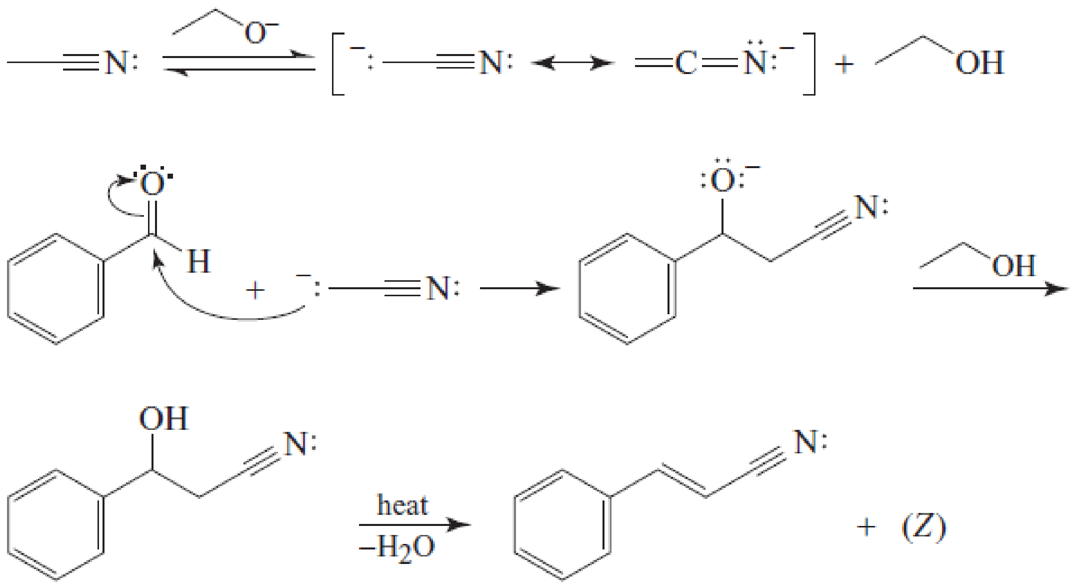
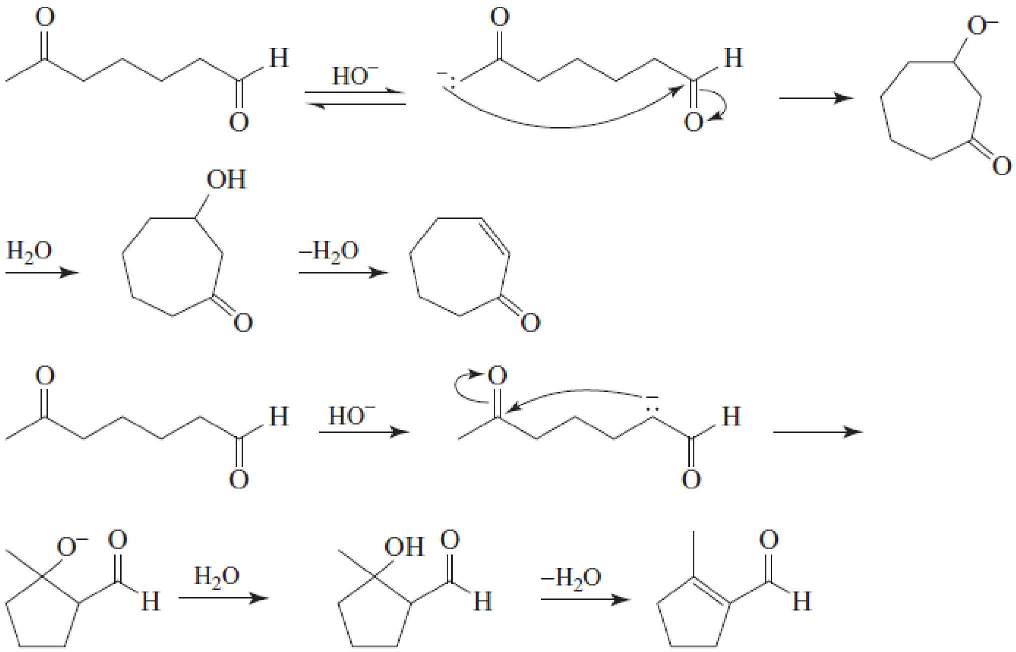
(a) 

(b) 

16.16



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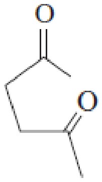
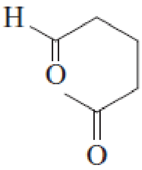
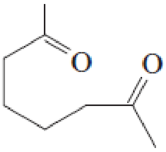
16.17

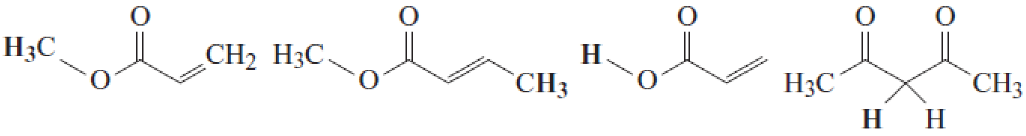
(a)  (b)  (c) 

Notice that starting compounds are drawn so as to indicate which atoms are involved in the cyclization reaction.

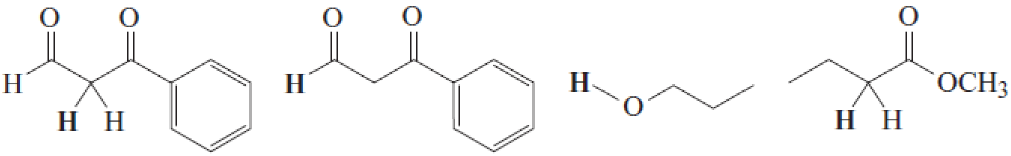
Review Problems

Enolates, Enols, and Carbonyl α-Carbon Reactivity

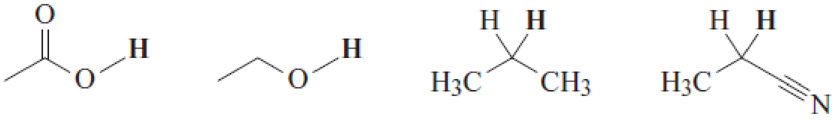
16.18

(a) 

1 2 4 3

(b) 

4 1 3 2

(c) 

4 3 1 2

16.19

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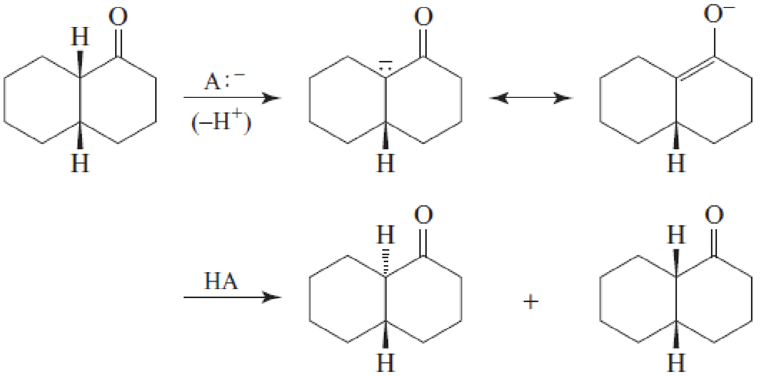
Abstraction of an α hydrogen at the ring junction yields an enolate anion that can then accept a proton to form either *trans*-1-decalone or *cis*-1-decalone. Since *trans*-1-decalone is more stable, it predominates at equilibrium.



(95%) *trans*-1-Decalone (more stable)

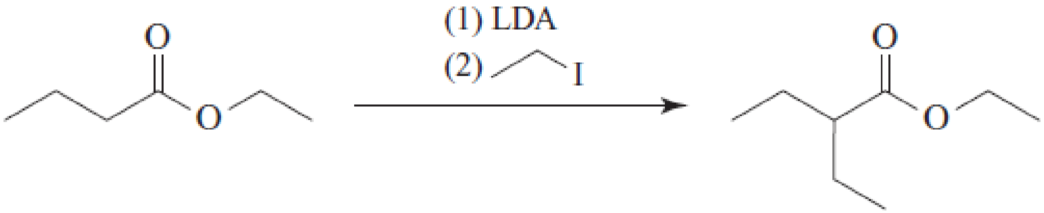
(5%) *cis*-1-Decalone (less stable)

16.20

In a polar solvent, such as water, the keto form is stabilized by solvation. When the interaction with the solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.

16.21

(a)



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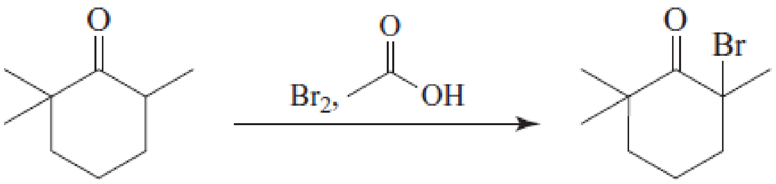
(b)



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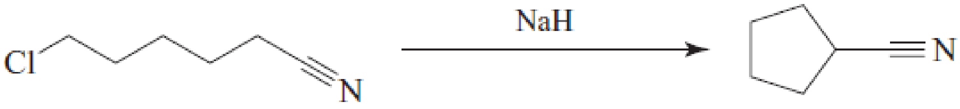

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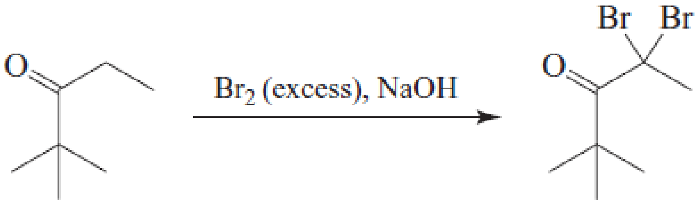

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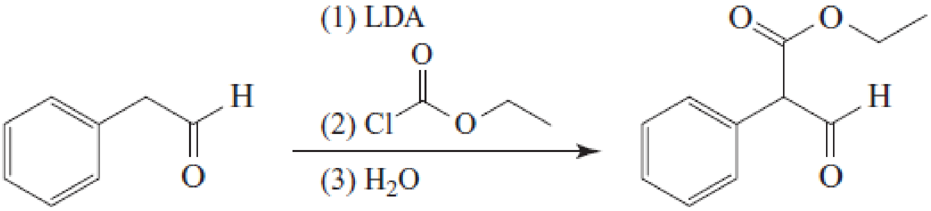

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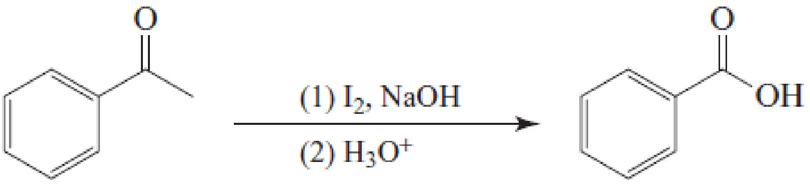

16.22

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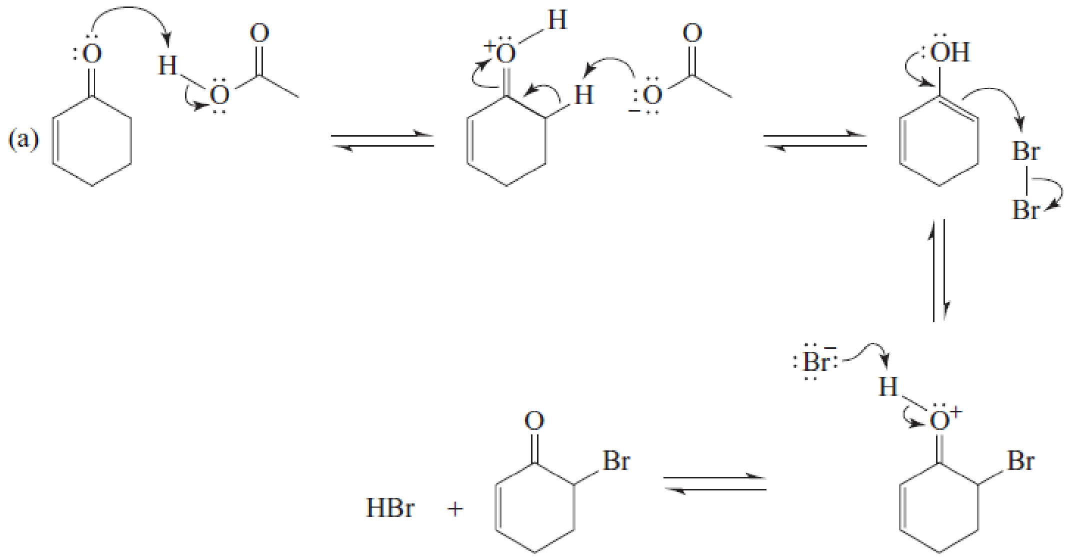

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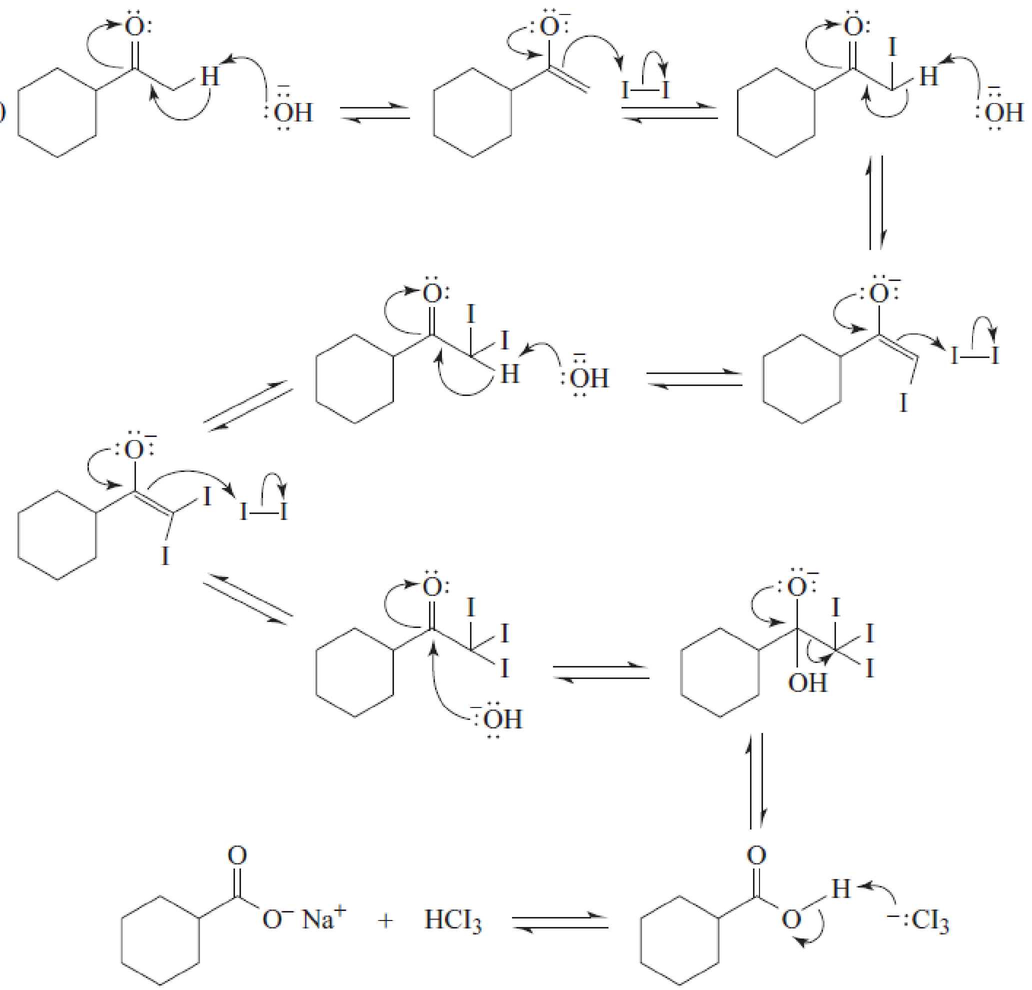

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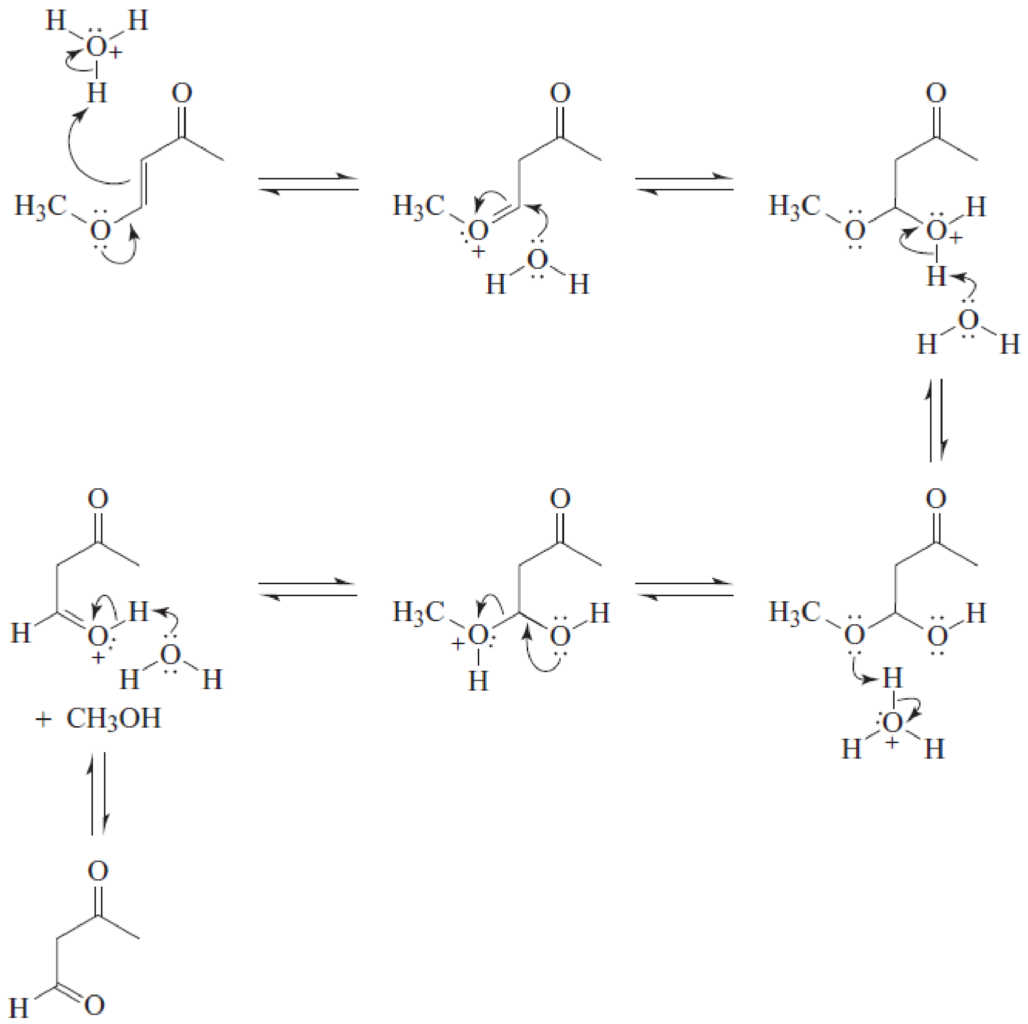
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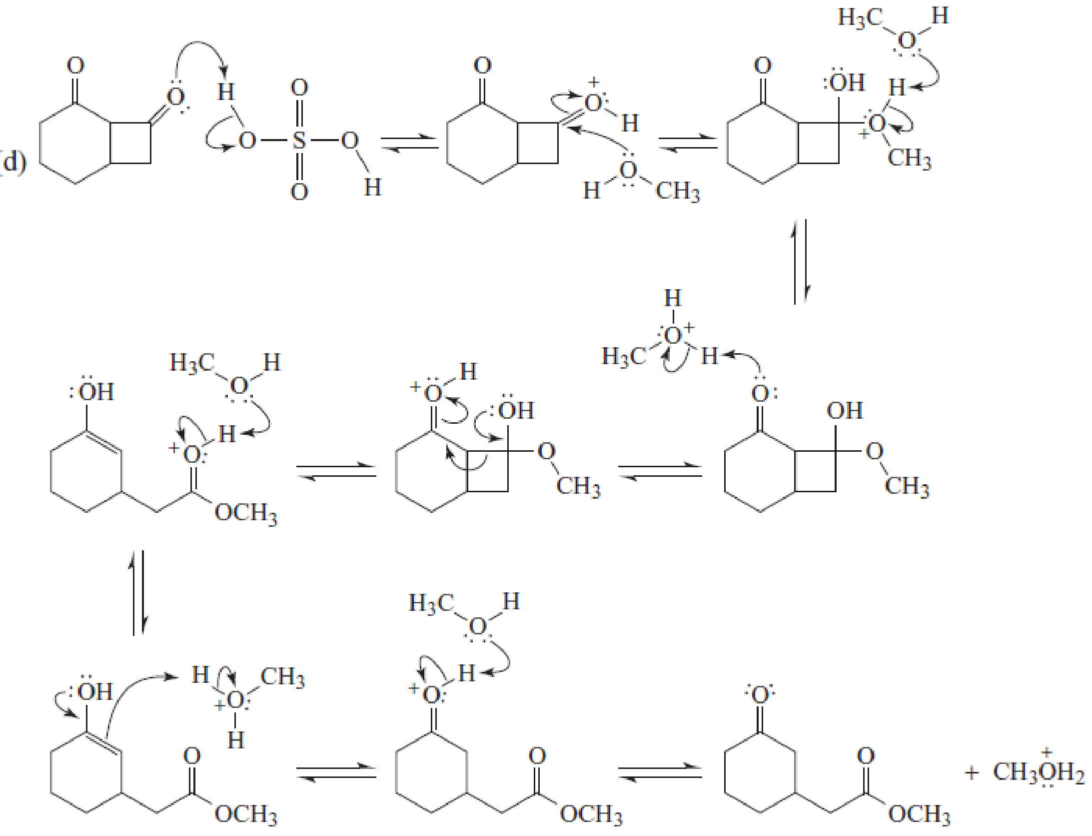

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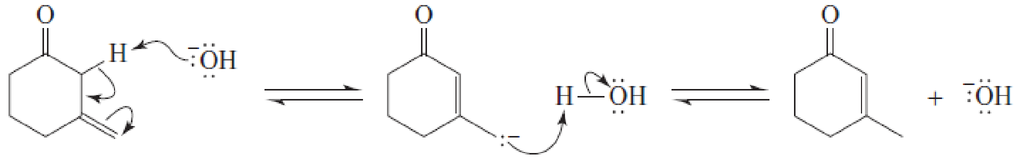

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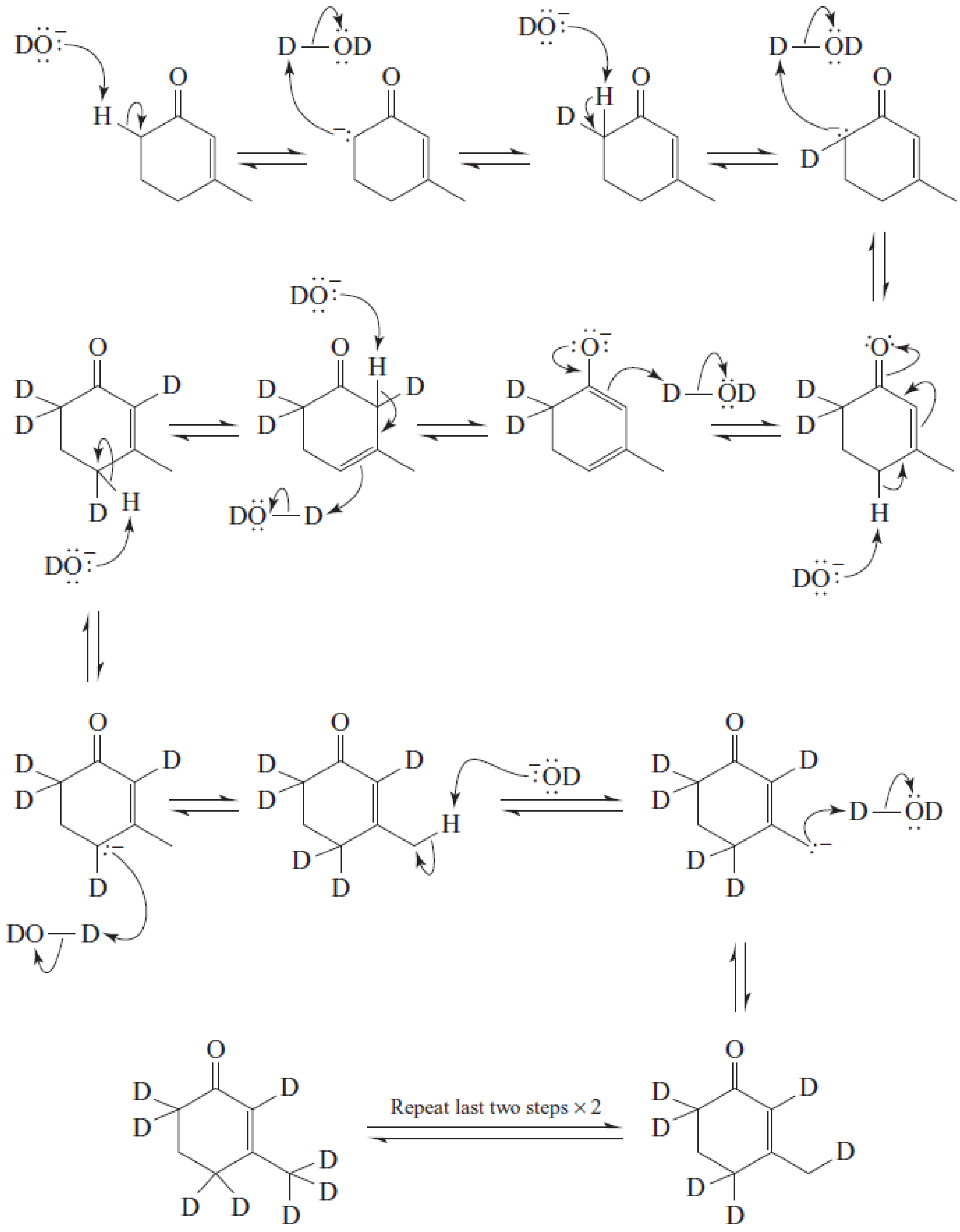

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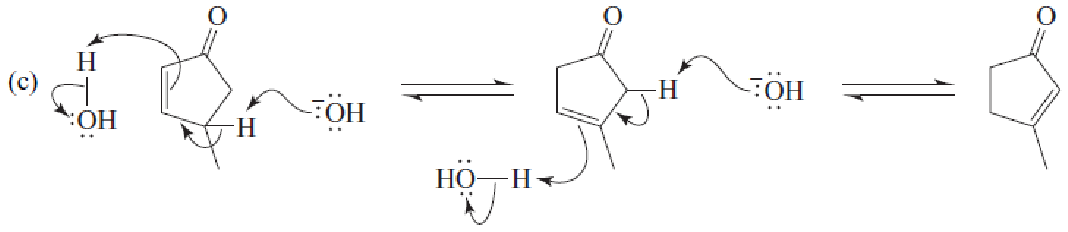
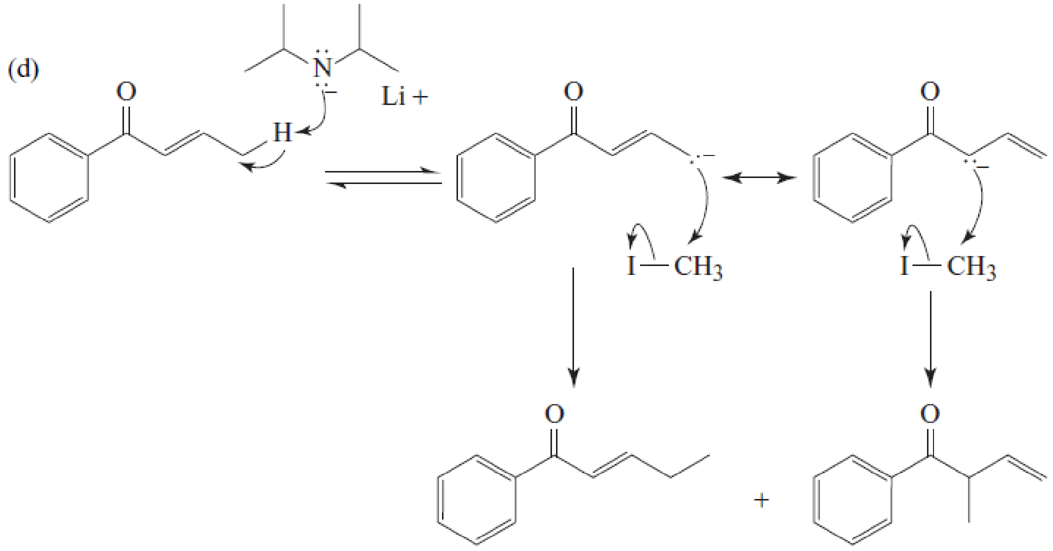
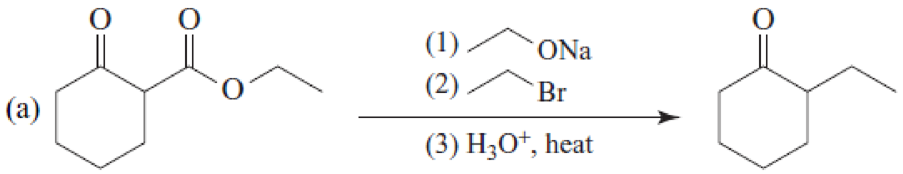
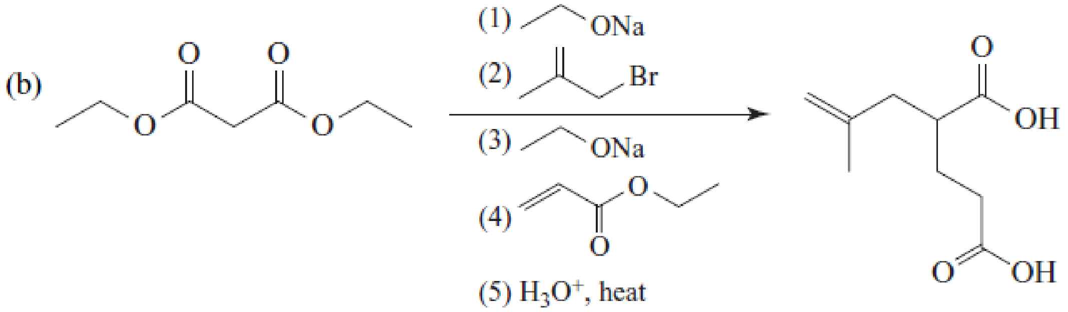




General Problems

16.24





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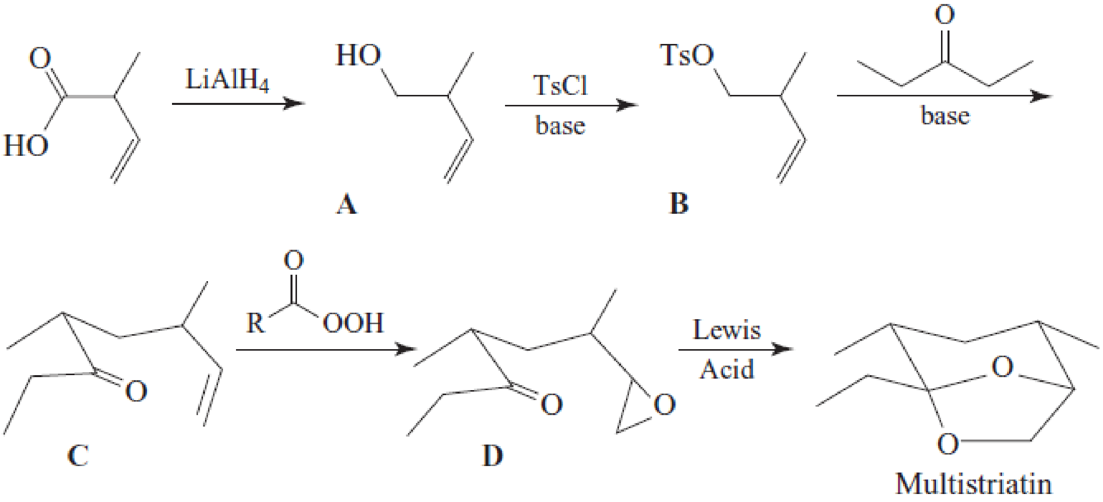
16.25



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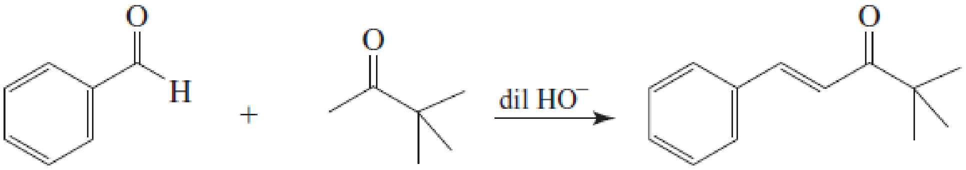
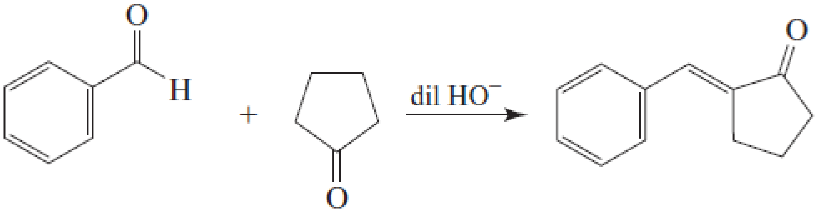
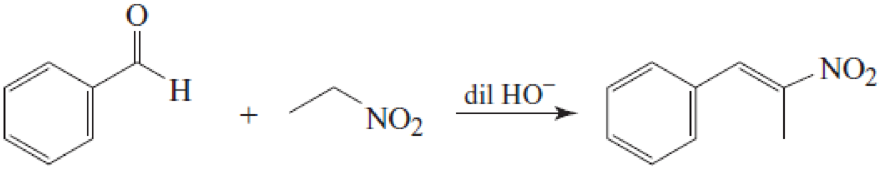
(a) 

(b) 

(c) 

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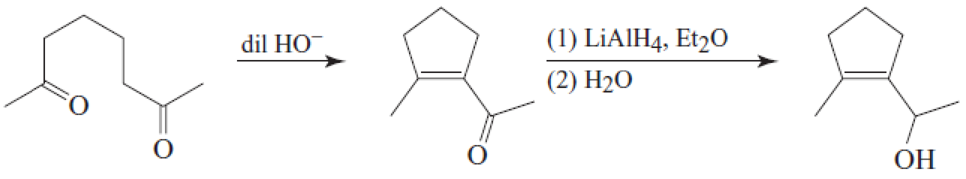
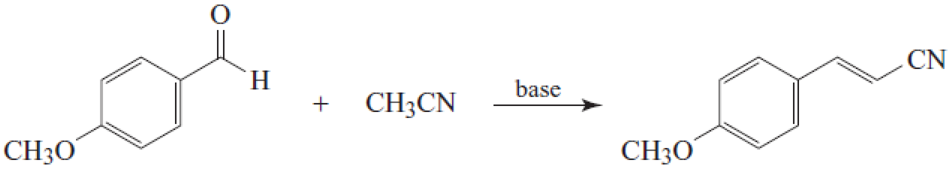
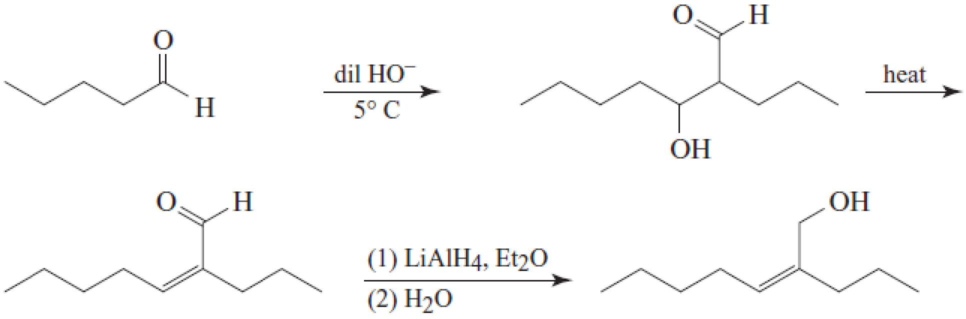
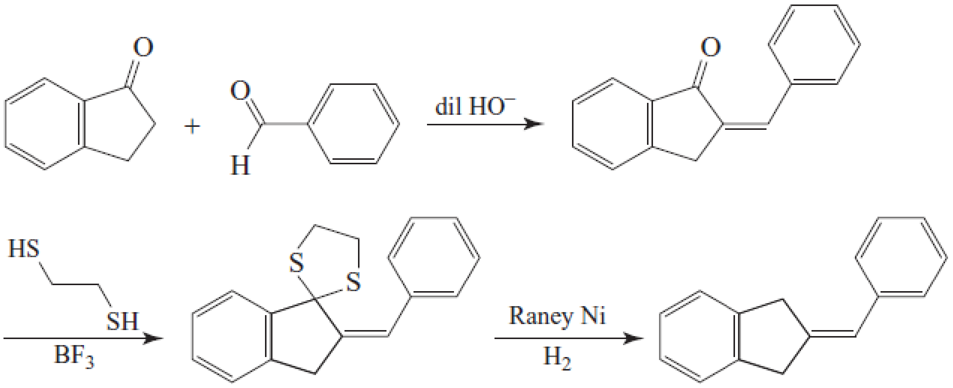
(d) 

(e) 

(f) 

(g) 

16.27

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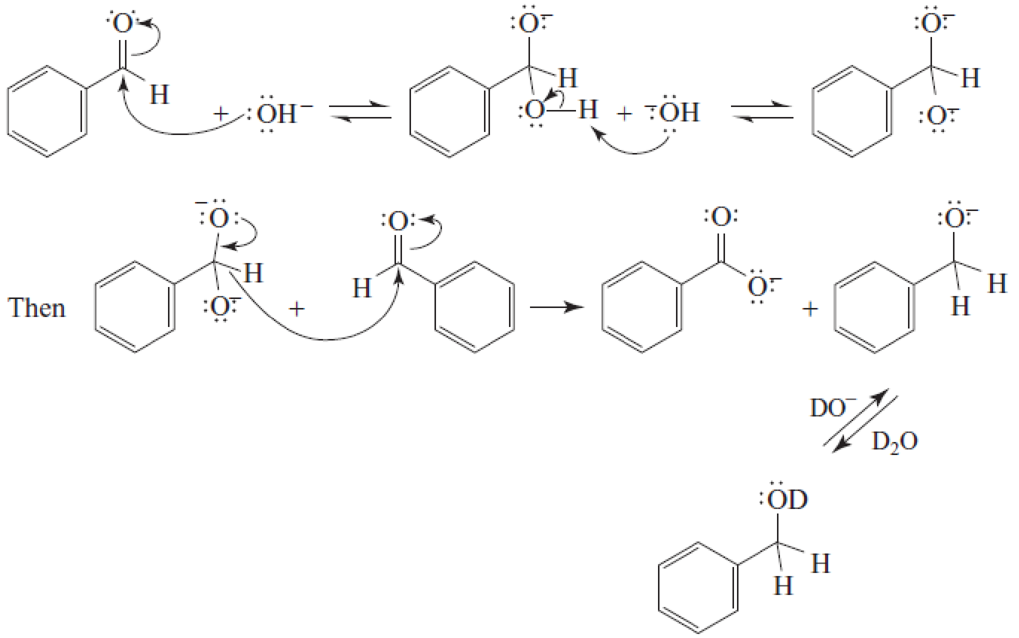
(a) The hydrogen atom that is added to the aldehyde carbon atom in the reduction must come from the other aldehyde rather than from the solvent. It must be transferred as a hydride ion and directly from molecule to molecule, since if it were ever a free species it would react immediately with the solvent. A possible mechanism is the following:



(b) Although an aldol reaction occurs initially, the aldol reaction is reversible. The Cannizzaro reaction, though slower, is irreversible. Eventually, all the product is in the form of the alcohol and the carboxylate ion.

16.28

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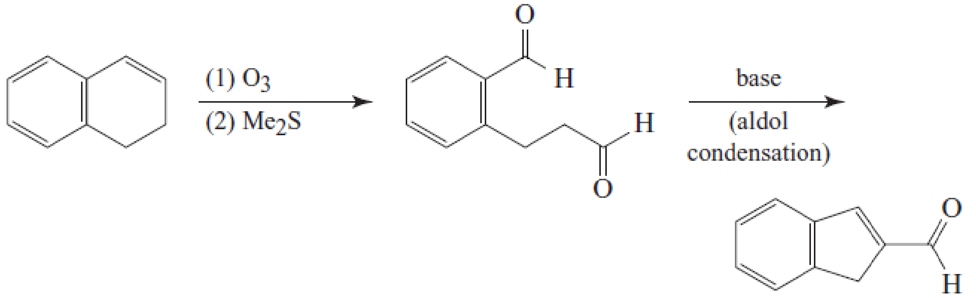
(a)



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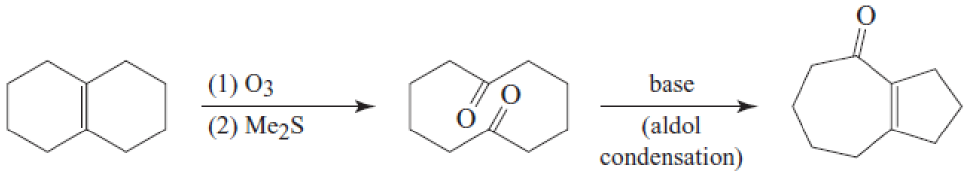

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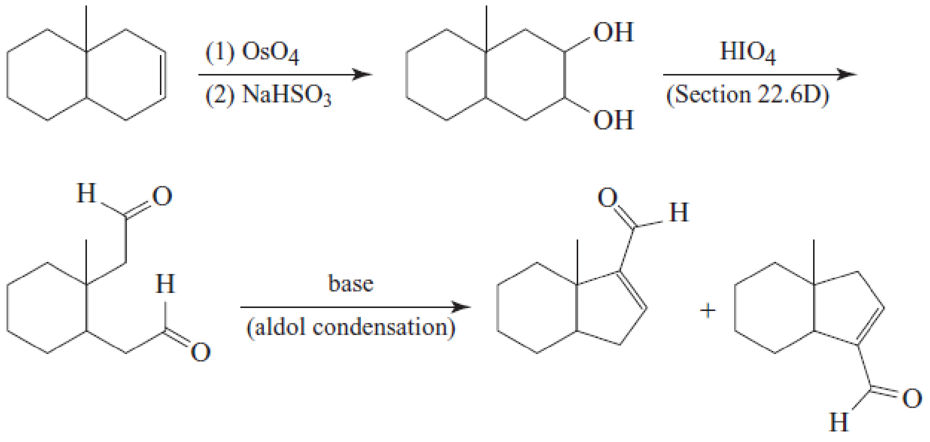

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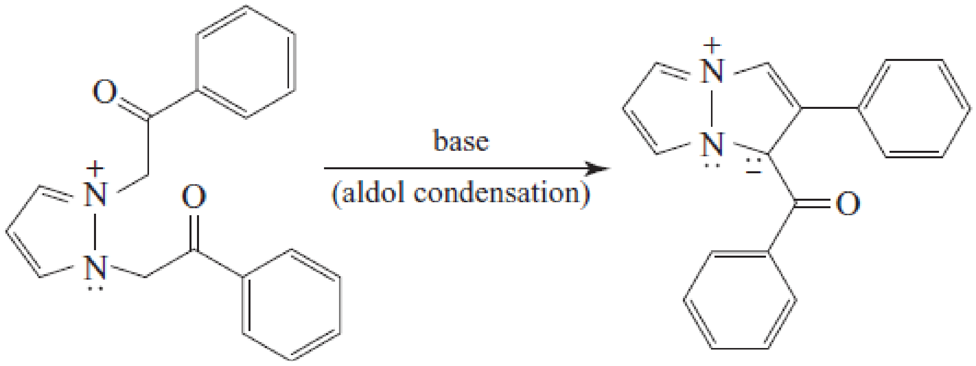

16.29

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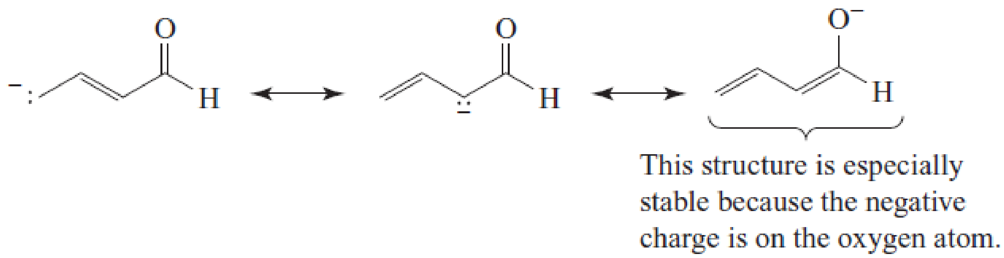
(a) The conjugate base is a hybrid of the following structures (cf. Rev. Prob. 19.30):



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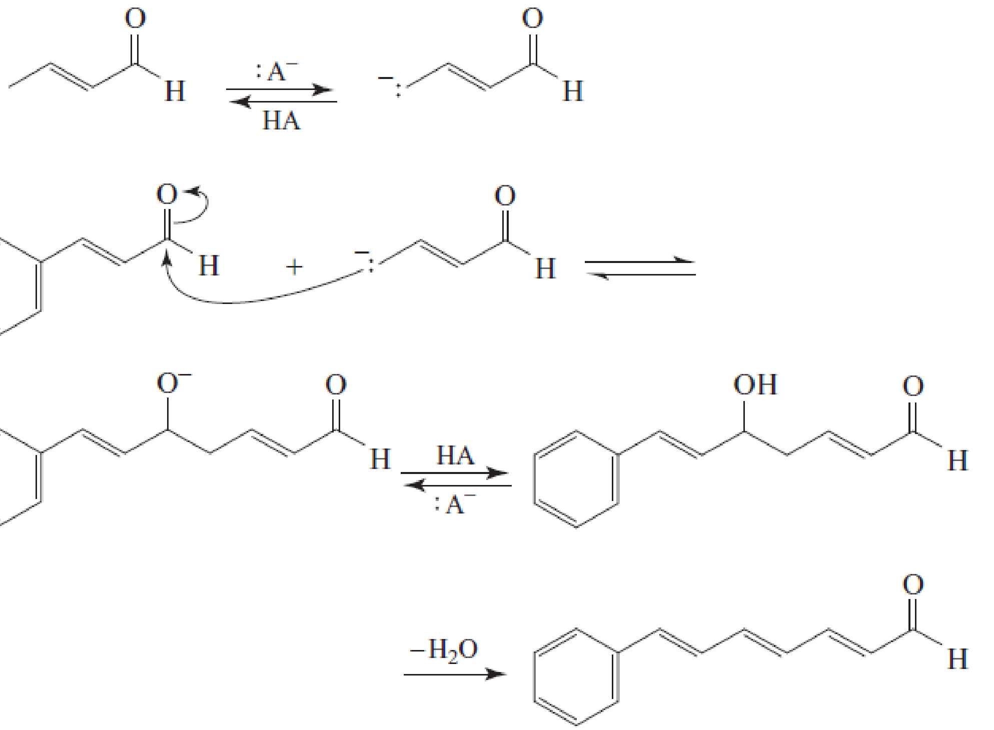

<H1> **ADDITIONAL OBJECTIVE QUESTIONS**

<H2> **Single Correct Choice Type**

1. **(d)** Mixed aldol is between different carbonyl groups and aldehyde is more reactive towards nucleophilic attack than ketone. It requires a strong base to abstract α H.

2. (c) It is Aldol reaction.

3. **(c)** It is Cannizaro reaction.
4. **(a)** It is Aldol condensation product.

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5. **(d)** The RDS is the transfer of hydride to carbonyl group.

6. **(d)** It is Aldol condensation.
7. (d) It is Aldol condensation product. The first reaction step involves ozonolysis resulting in ketone.
8. **(c)** It is Iodoform test, C of iodoform comes from the active methylene position.
9. **(c)** It is aldol condensation.
10. (d) Reactants are cyclohexanone and benzaldehyde.
11. **(c)** X is 2-hydroxybenzaldehyde which then undergoes Cannizaro reaction.
12. **(b)** Acetaldehyde doesn't give Cannizaro as it has α H atoms.
13. **(b)** Cannizzaro results in benzyl alcohol and benzoic acid from benzaldehyde.
14. **(b)** It is Aldol reaction.
15. **(a)** It is Cannizzaro reaction, hydroxide will attack the more electron deficient formaldehyde carbon and turn it into acid.
16. (c) It is aldol condensation reaction.
17. **(d)** Nucleophilic attack will take place more readily at the aldehyde C than ketone C.
18. (c) It is aldol condensation reaction.
19. **(c)**
20. (b) Correction!! Reactants are ethanal and butanal. All the other three products are possible.
21. **(b)** In forming B from A, the right vertical bond of the middle ring will be cleaved by ozonolysis to yield two aldehyde groups, which then undergo Cannizzaro to yield an alcohol and carboxylic group. Further dehydration takes place from the two groups to form ester.
22. **(c)** Enol is formed in the acid catalyzed aldol.
23. **(d)** For self-condensation, α H is required.
24. **(d)** It is aldol condensation reaction.
25. **(d)** It is aldol condensation reaction.
26. **(a)** In Cannizzaro reaction, the hydroxide attacks the carbonyl group which produces the carboxylic acid.

<H2> Linked Comprehension Type

1. **(b)** J is benzaldehyde and it undergoes Cannizzaro to form benzyl alcohol and L (Benzoic acid). K is acetophenone and it undergoes aldol condensation to form M. I can be obtained by retrosynthetic analysis of the ozonolysis reaction.
2. **(a)**
3. (d)
4. **(b)** Since P undergoes iodoform, it must have a methyl attached to carbonyl, thus possible options are a and b. In forming Q, in the dehydration step, the carbocation formed upon removal of water, undergoes EAS on the benzene ring. The product R formed upon ozonolysis undergoes aldol hence it must have α H which eliminates option a in Q.4. for reactant P.

5. (a)
6. (b)

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7. **(b)** B is Ethanal while C is Benzaldehyde (from respective retrosynthetic analysis). Thus we can get A.
8. **(b)** Benzaldehyde gives negative Fehling test as it lacks α H.
9. **(c)** D is cyanohydrin formed by nucleophilic addition of cyanide to the carbonyl group, while E involves hydrolysis of cyanide to form carboxylic acid followed by dehydration.
10. **(d)** Only d produces two products having 6 carbons each in the ozonolysis reaction.
11. (b) It is aldol condensation product of cyclohexanone.
12. **(d)** D is cyclohexane formed by Clemenson reduction.

<H2> Integer Type

1. (3) Two possible by attack from the two alpha position of ketone on aldehyde and one product from attack of alpha position of aldehyde on ketone.

2. **(8)** A is acetophenone which then undergoes aldol condensation.
3. **(1)** X is vicinal diol, Y is hexanedial and it then undergoes aldol to yield only one type of product.
4. **(3)** Cross aldol can take place from the 4 possible α H position but the α position having methyl group attached to it will not give condensation product as it would lack a H atom in the aldol product.
5. **(3)** It involves three aldol and one Cannizzaro.
6. (1) Y is cyclodeca-1,6-dione, which undergoes aldol condensation to yield only one type of product.

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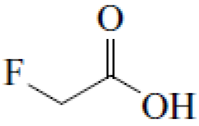
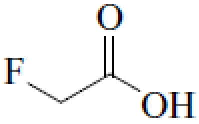
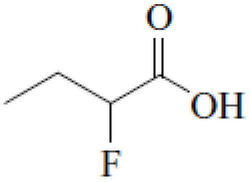
Chapter 17: Carboxylic Acids and Their Derivatives

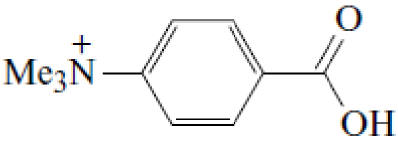
Practice Problems

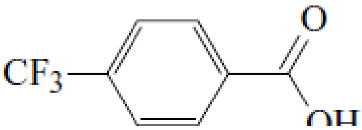
17.1

(a)  (F— is more electronegative than H—)

(b)  (F— is more electronegative than Cl—)

(c)  (F— is closer to $—CO_2H$)

(d)  [$Me_3\overset{+}{N}$— is more electronegative than H—]

(e)  (CF_3— is more electronegative than CH_3—)

17.2

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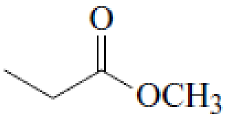
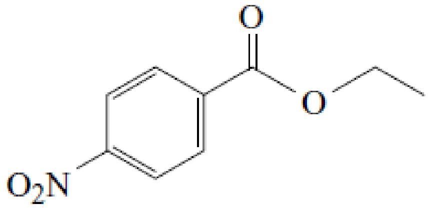
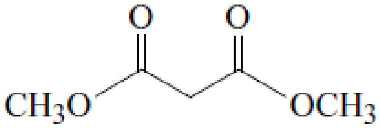
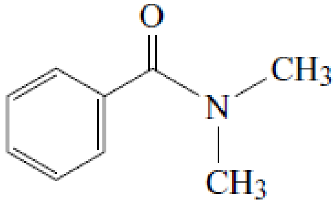
(a) 

(b) 

(c) 

(d) 

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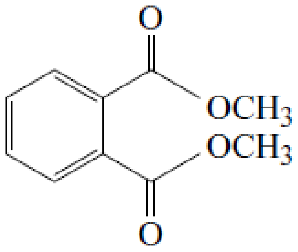
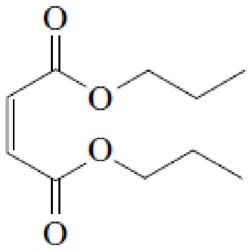
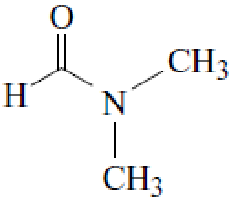
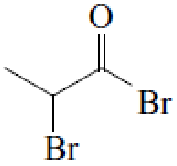
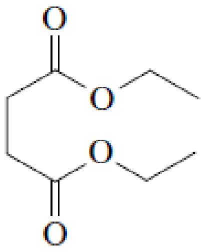
(f) 

(g) 

(h) 

(i) 

(j) 

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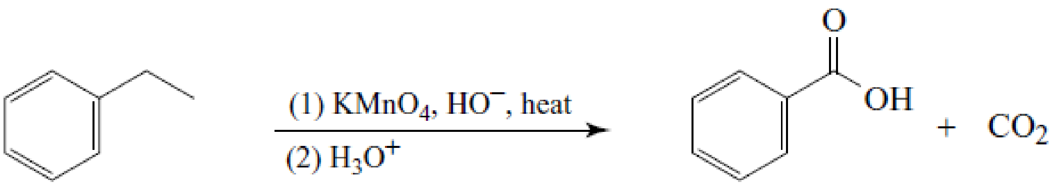

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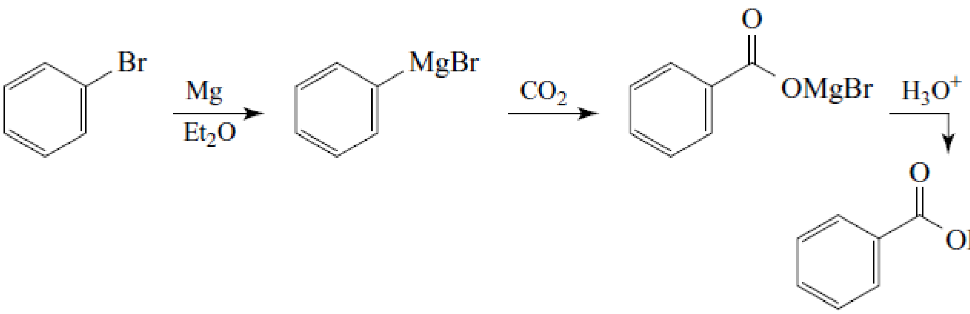

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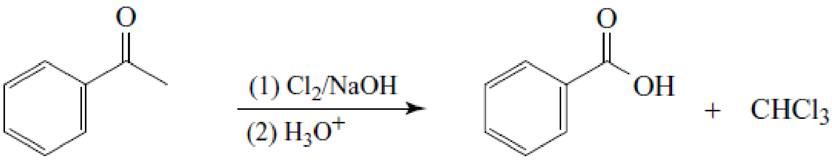

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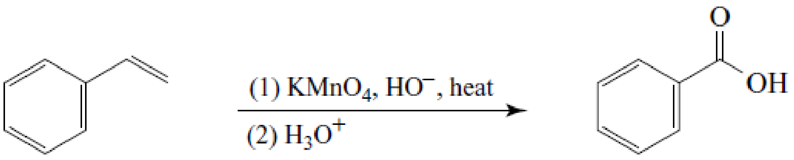

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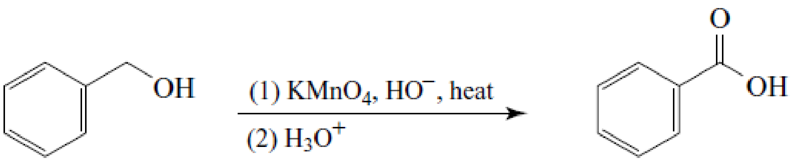

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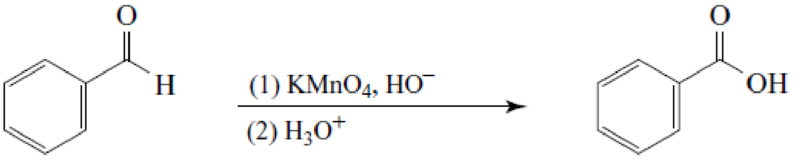

17.4

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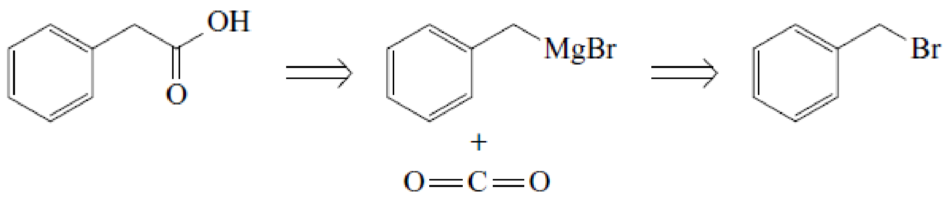
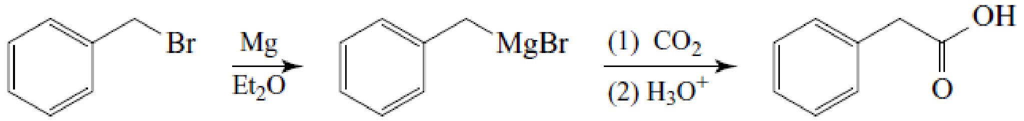
These syntheses are easy to see if we work backward using a retrosynthetic analysis before writing the synthesis.

(a) ***Retrosynthetic analysis***



Synthesis



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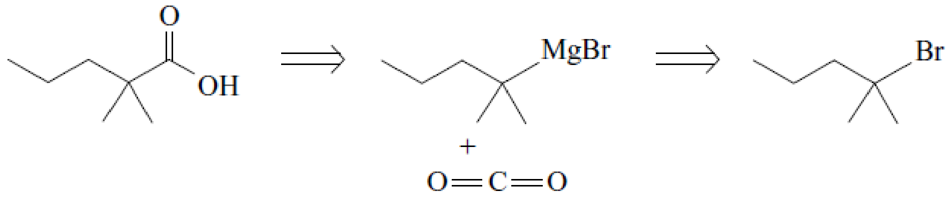
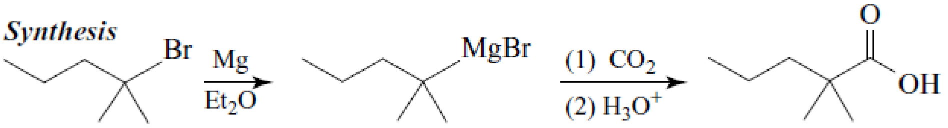
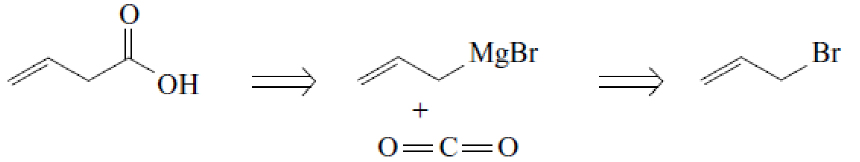
(b) ***Retrosynthetic analysis***



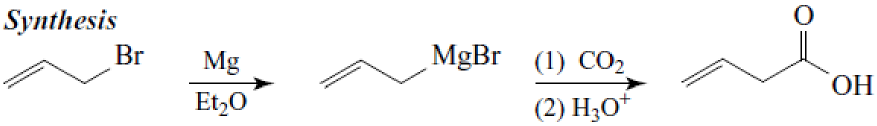
Synthesis



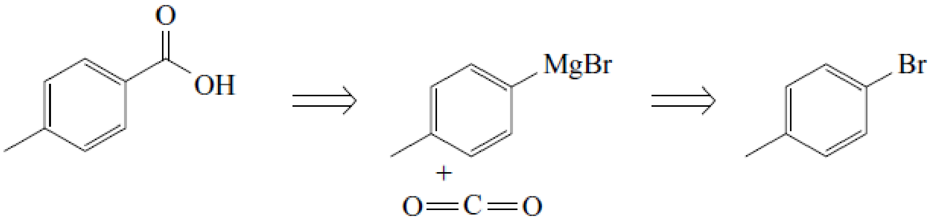
(c) ***Retrosynthetic analysis***



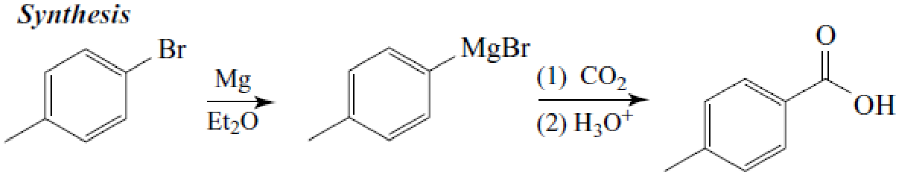
Synthesis



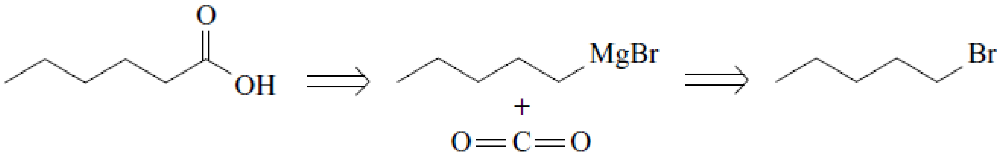
(d) ***Retrosynthetic analysis***



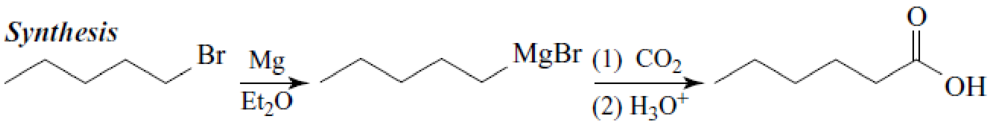
Synthesis



(e) ***Retrosynthetic analysis***



Synthesis



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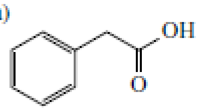
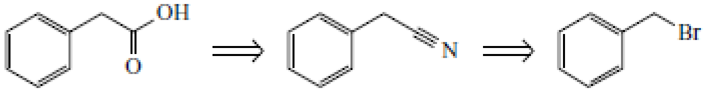
17.5

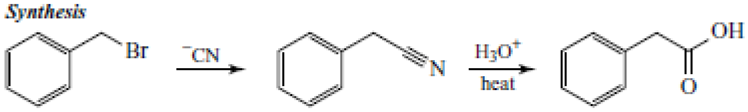
(a)

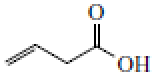


Retrosynthetic analysis



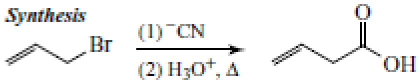
Synthesis





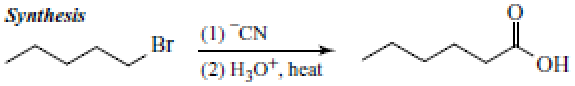
Retrosynthetic analysis

Synthesis



Retrosynthetic analysis

Synthesis



(b) A nitrile synthesis. Preparation of a Grignard reagent from HO would not be possible because of the presence of the acidic hydroxyl group.

17.6

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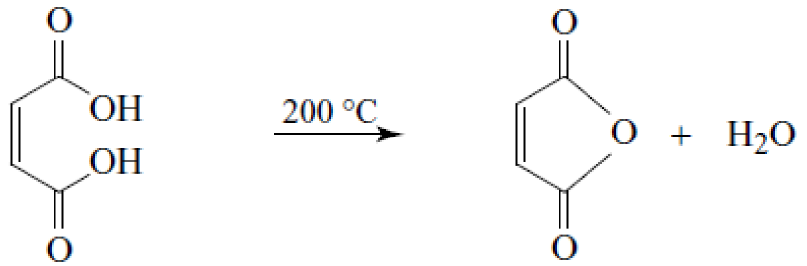
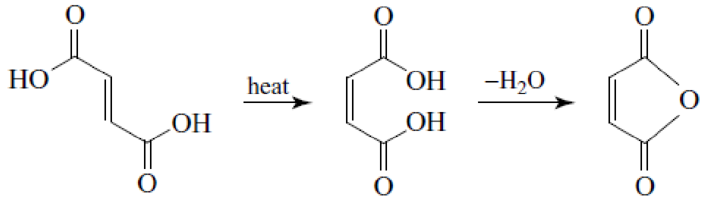
Since maleic acid is a cis dicarboxylic acid, dehydration occurs readily:



Maleic acid   Maleic anhydride

Being a trans dicarboxylic acid, fumaric acid must undergo isomerization to maleic acid first. This isomerization requires a higher temperature.



Fumaric acid

17.7

The labeled oxygen atom should appear in the carboxyl group of the acid. (Follow the reverse steps of the mechanism in Section 17.7A of the text using $H_2{}^{18}O$.)

17.8

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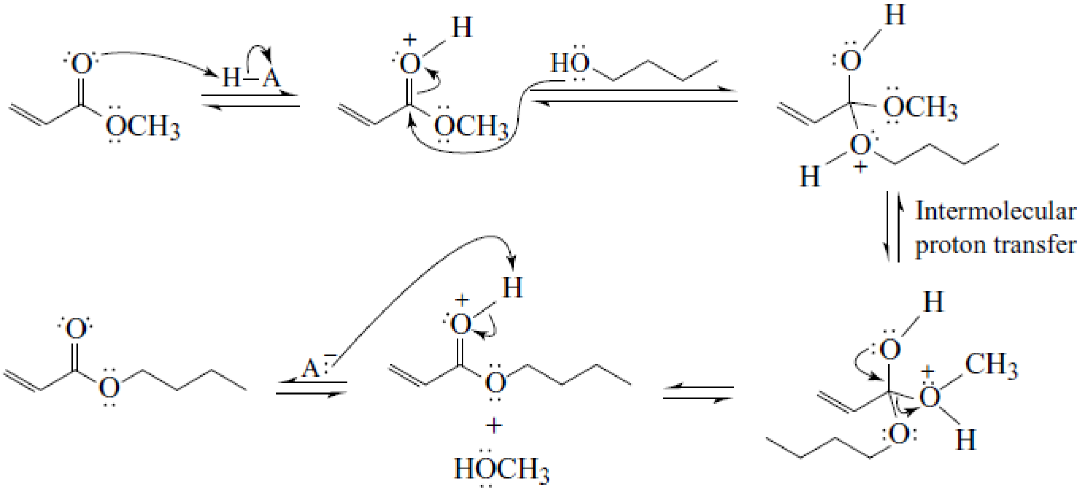
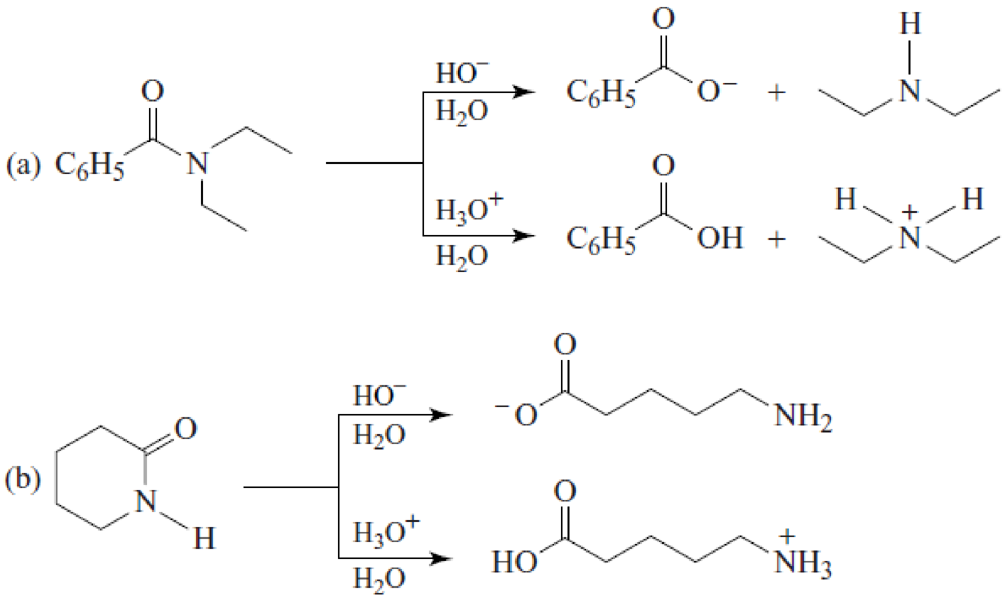


17.9



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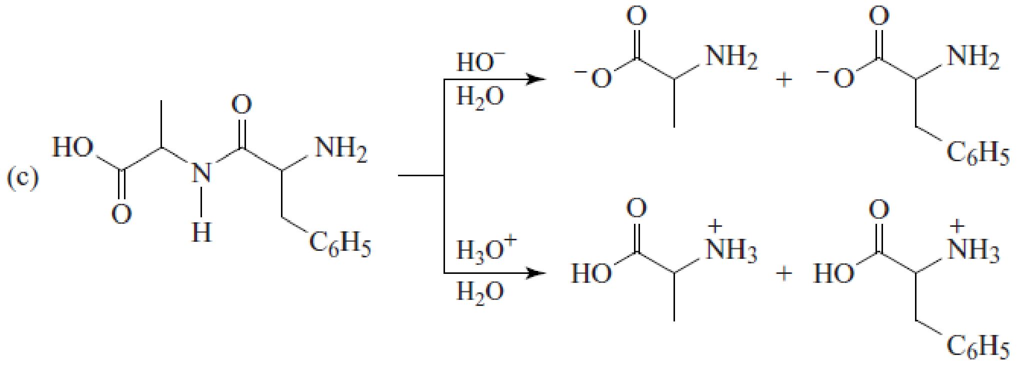
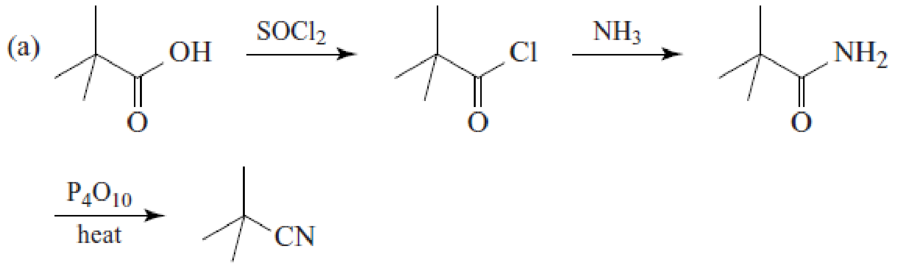
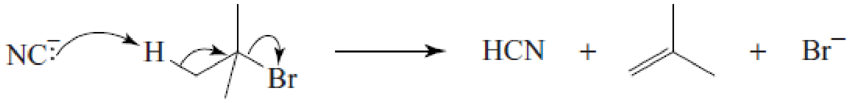


17.10



(b) An elimination reaction would take place because $^{-}$CN is a strong base, and the substrate is a 3° alkyl halide.



17.11

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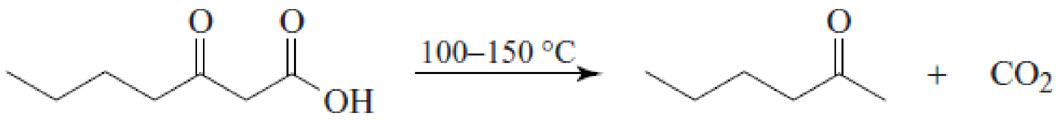
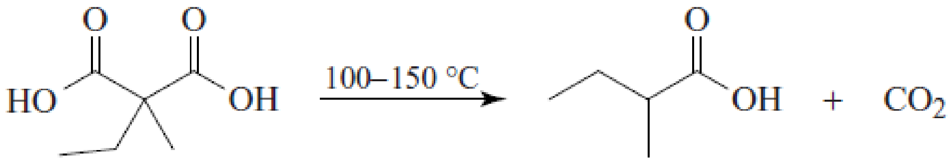
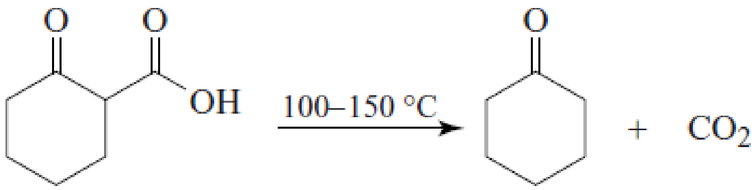
(a) By decarboxylation of a *β*-keto acid:



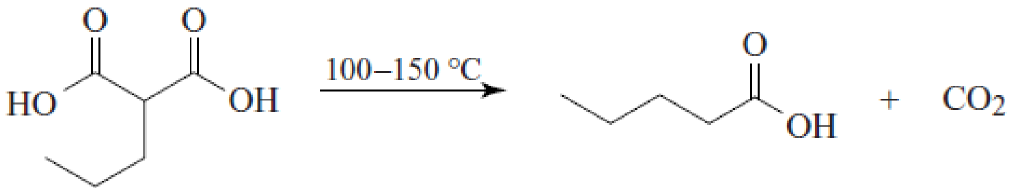
(b) By decarboxylation of a *β*-keto acid:



(c) By decarboxylation of a *β*-keto acid:



(d) By decarboxylation of a *β*-keto acid:



Review Problems

Structure and Nomenclature

17.12

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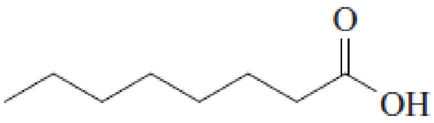
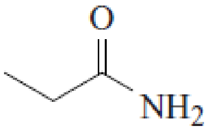
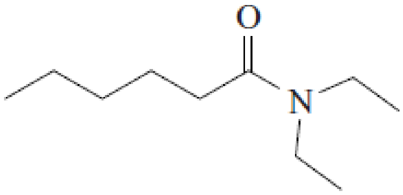
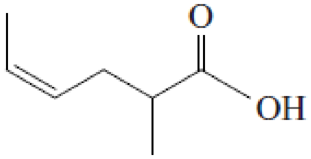
(a) 

(b) 

(c) 

(d) 

[the (*Z*) isomer]

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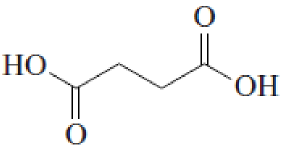
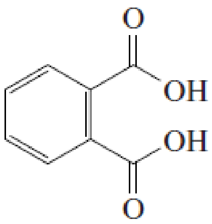
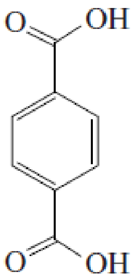
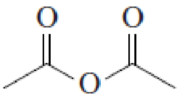
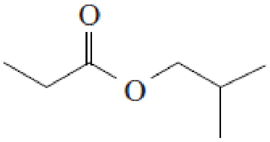
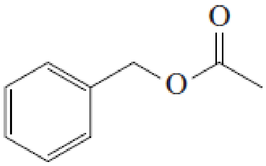
(e) 

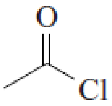
(f) 

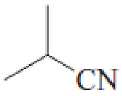
(g) 

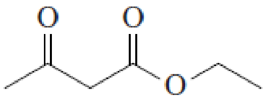
(h) 

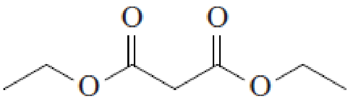
(i) 

(j) 

(k) 

(l) 

(m) 

(n) 

17.13

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(a) Benzoic acid

(b) Benzoyl chloride

(c) Acetamide or ethanamide

(d) Acetic anhydride or ethanoic anhydride

(e) Benzyl benzoate

(f) Phenyl propanoate or phenyl propionate

(g) Isopropyl acetate or 1-methylethyl ethanoate

(h) Acetonitrile or ethanenitrile

17.14

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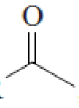
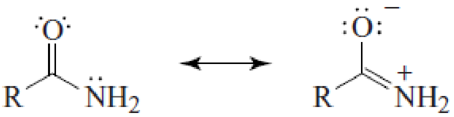
Alkyl groups are electron releasing; they help disperse the positive charge of an alkyl-ammonium salt and thereby help to stabilize it.

$$R\ddot{N}H_2 + H_3O^+ \longrightarrow R{\rightarrow}NH_3^+ + H_2O$$

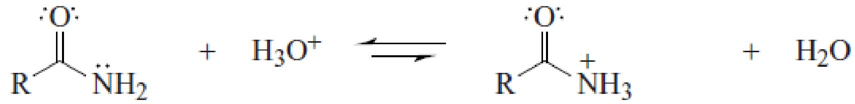
Stabilized by electron-releasing alkyl group

Consequently, alkylamines are somewhat stronger bases than ammonia.

Amides, on the other hand, have acyl groups, R , attached to nitrogen, and acyl groups are electron withdrawing. They are especially electron withdrawing because of resonance contributions of the kind shown here,



This kind of resonance also *stabilizes* the amide. The tendency of the acyl group to be electron withdrawing, however, *destabilizes* the conjugate acid of an amide, and reactions such as the following do not take place to an appreciable extent.



Stabilized by resonance

Destabilized by electron-withdrawing acyl group

17.15

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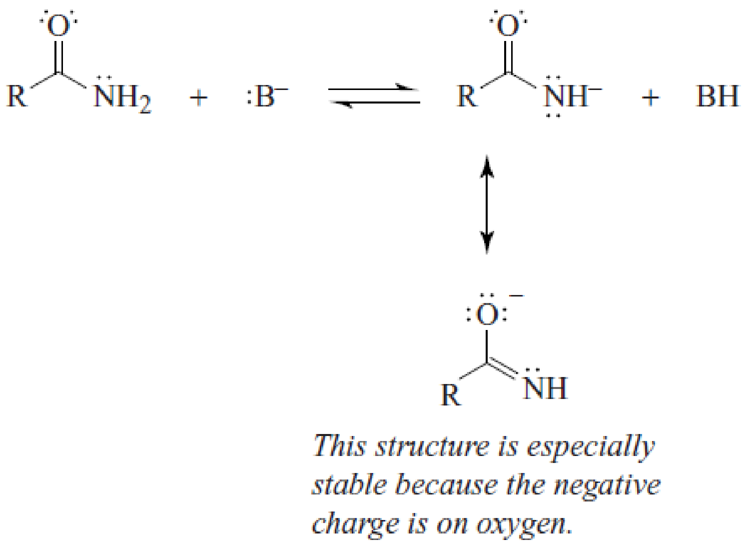
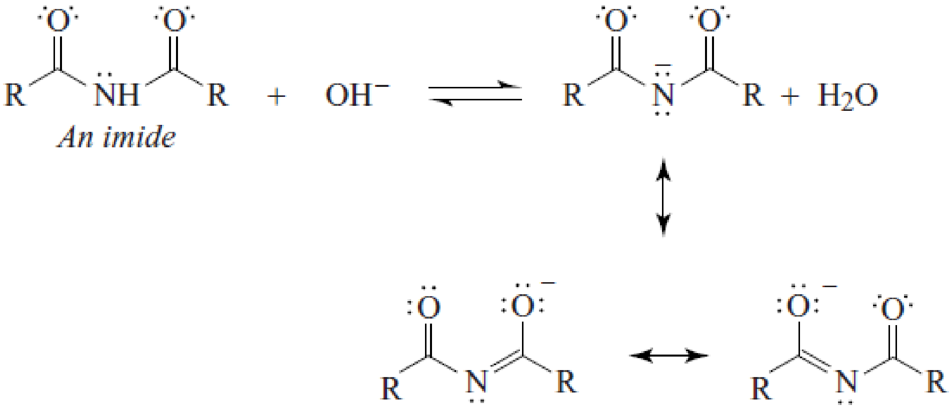
(a) The conjugate base of an amide is stabilized by resonance.



There is no resonance stabilization for the conjugate base of an amine, RNH^-.

(b) The conjugate base of an imide is stabilized by additional resonance structures,



Functional Group Transformations

17.16

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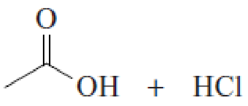
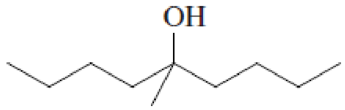
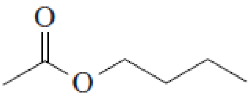
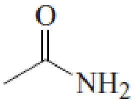
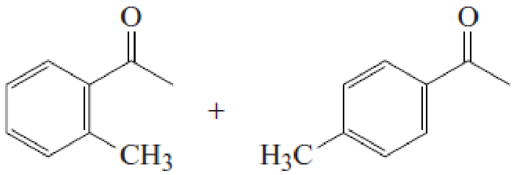
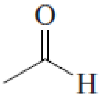
(a) 

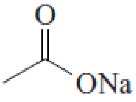
(b) 

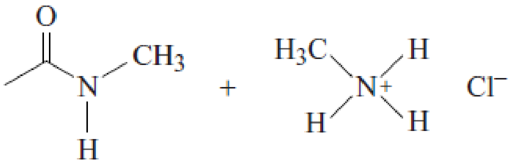
(c) 

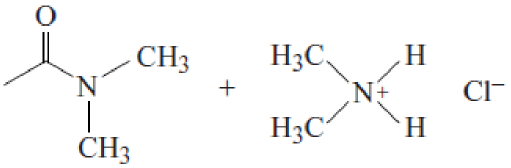
(d) 

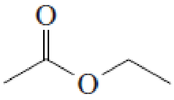
(e) 

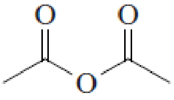
(f) 

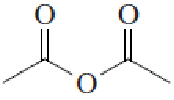
(g) 

(h) 

(i) 

(j) 

(k) 

(l) 

17.17

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(a) $CH_3CONH_2 + CH_3CO_2^- \overset{+}{N}H_4$

(b) $2\ CH_3CO_2H$

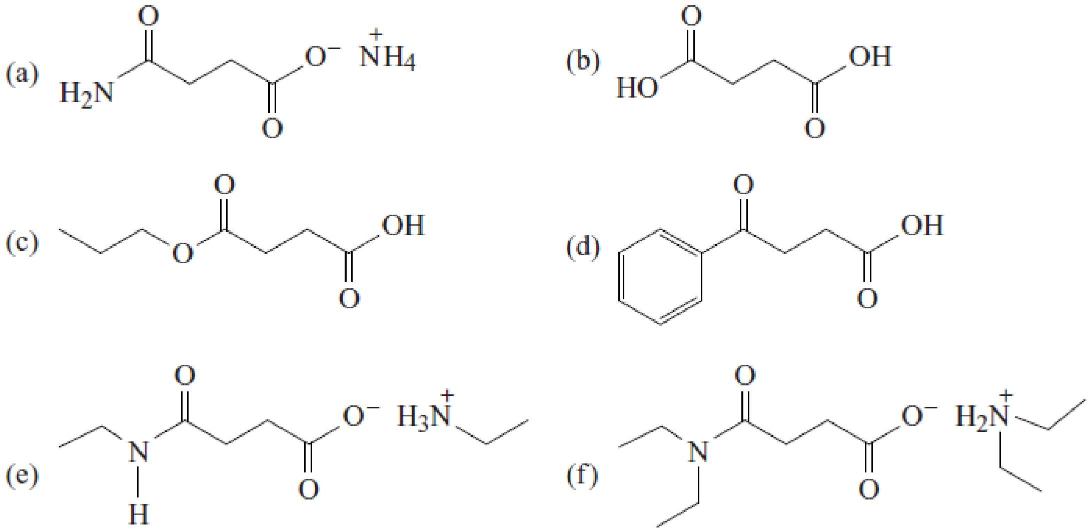
(c) $CH_3CO_2CH_2CH_2CH_3 + CH_3CO_2H$

(d) $C_6H_5COCH_3 + CH_3CO_2H$

(e) $CH_3CONHCH_2CH_3 + CH_3CO_2^-\ CH_3CH_2\overset{+}{N}H_3$

(f) $CH_3CON(CH_2CH_3)_2 + CH_3CO_2^-(CH_3CH_2)_2\overset{+}{N}H_2$

17.18



17.19

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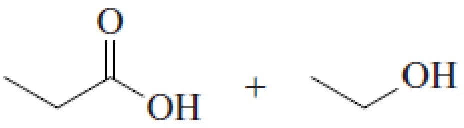
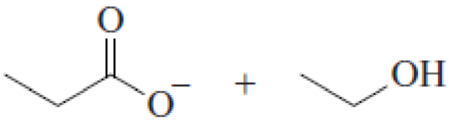
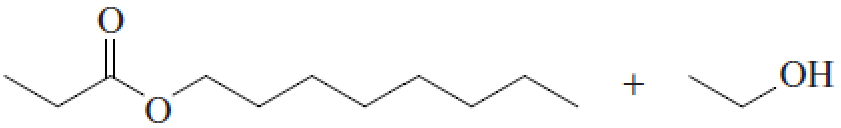
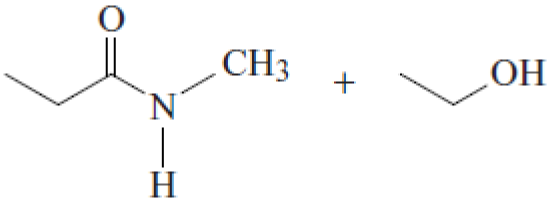
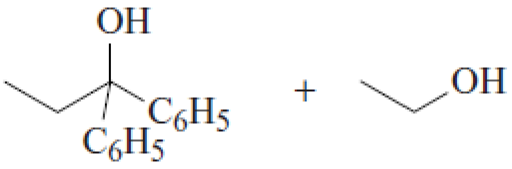
(a) 

(b) 

(c) 

(d) 

(e)

(f) 

17.20

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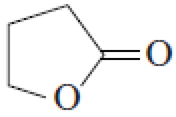
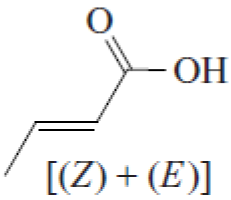
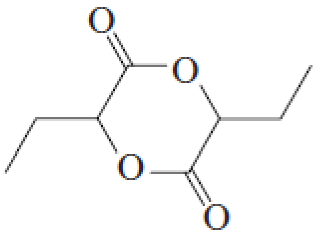
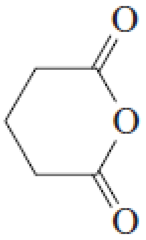
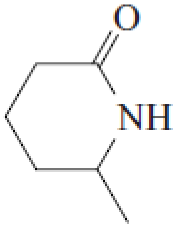
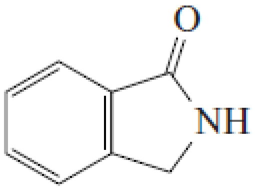
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

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General Problems

17.21

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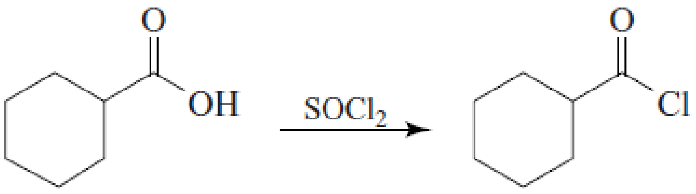
(a)



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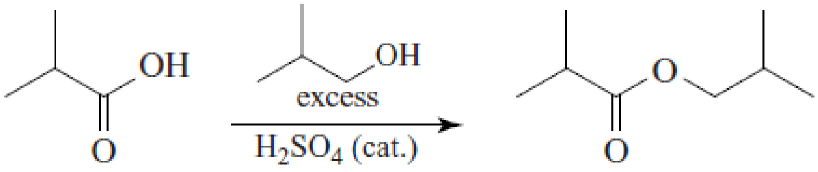

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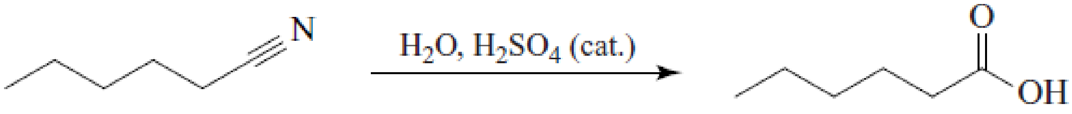
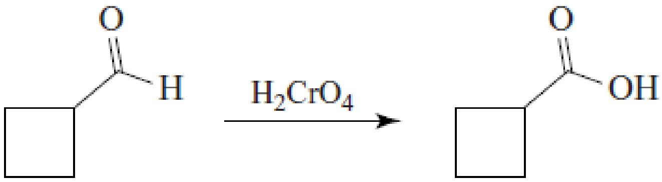


(d)



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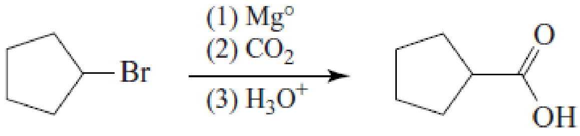
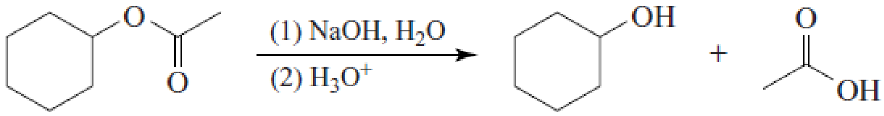
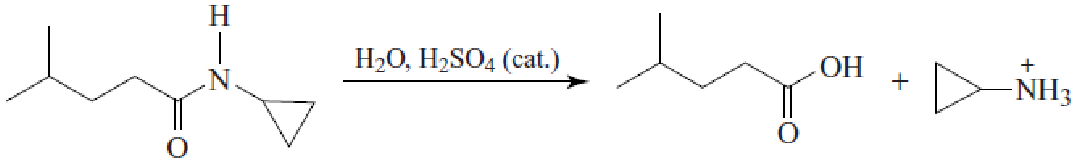
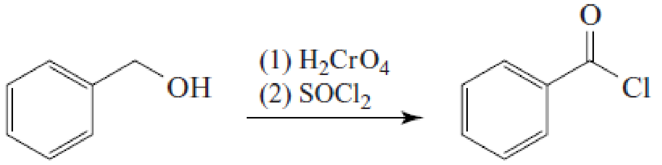
(e) 

(f) 

(g) 

(h) 

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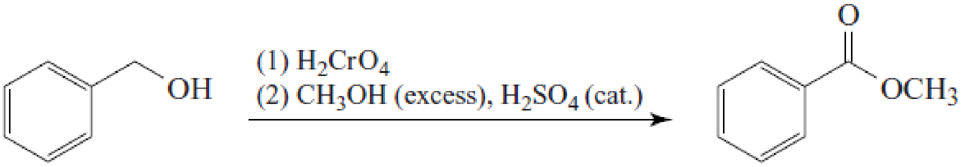
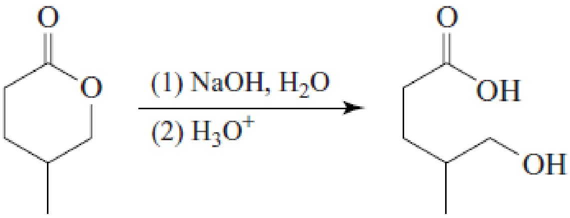
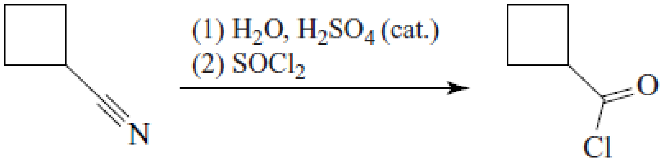
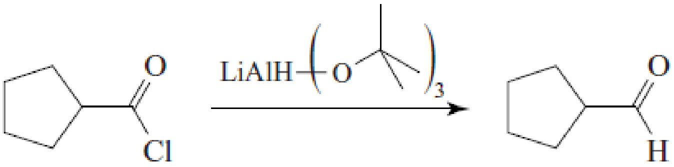
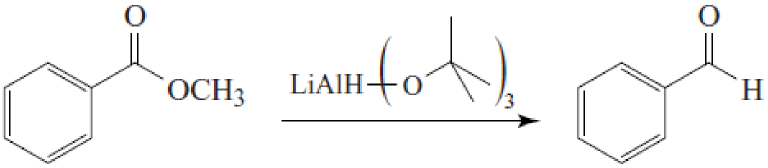
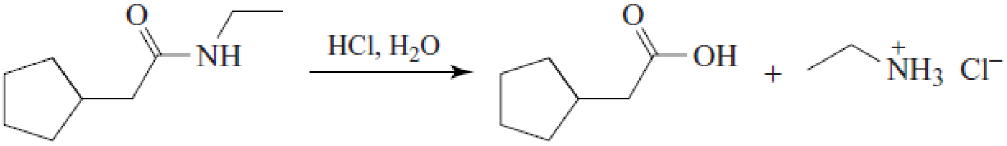
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

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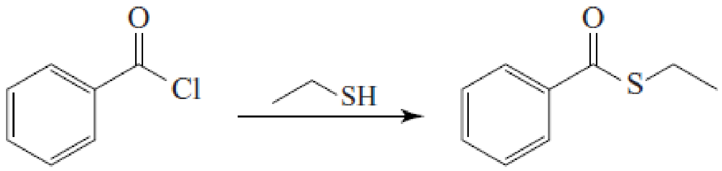
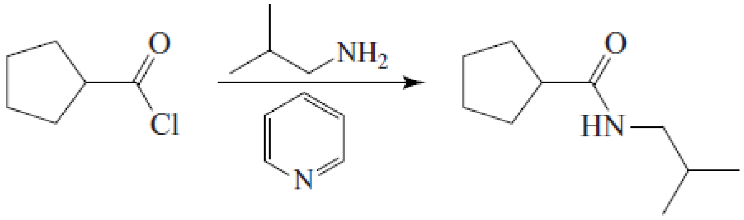
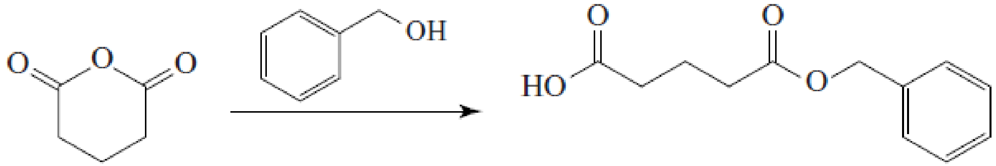
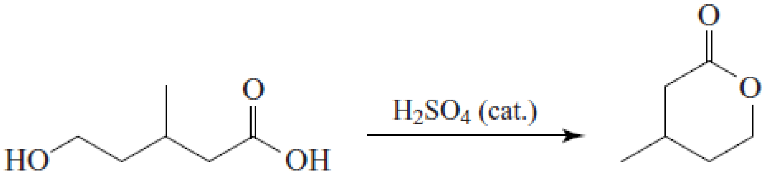
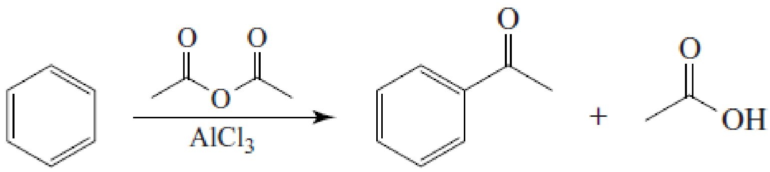
(a) 

(b) 

(c) 

(d) 

(e) 

17.24

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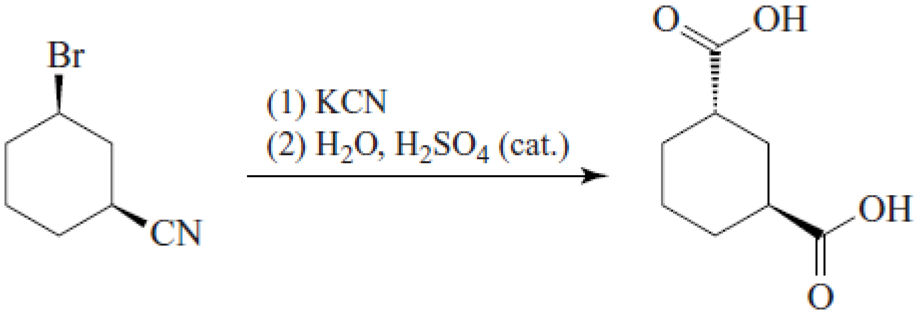

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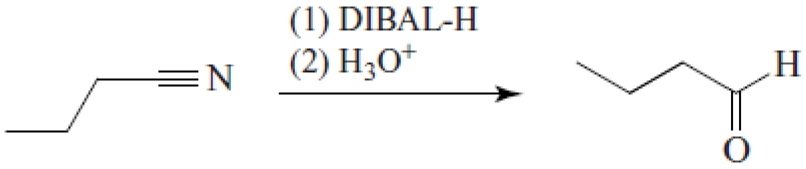

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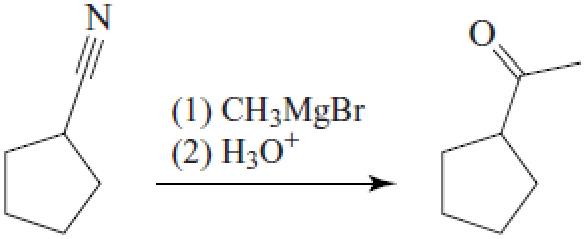

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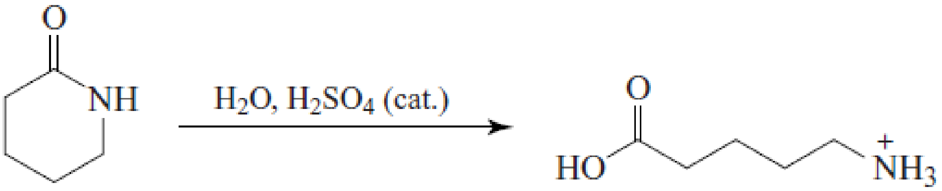

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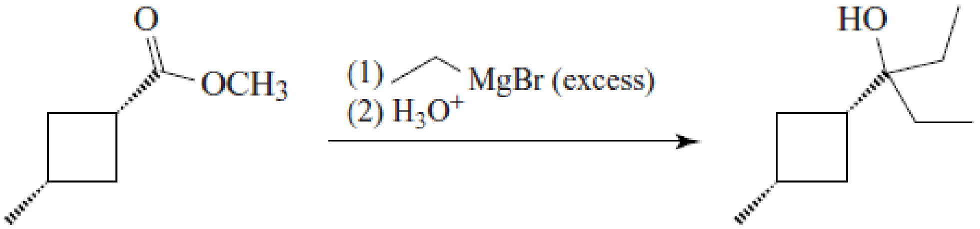

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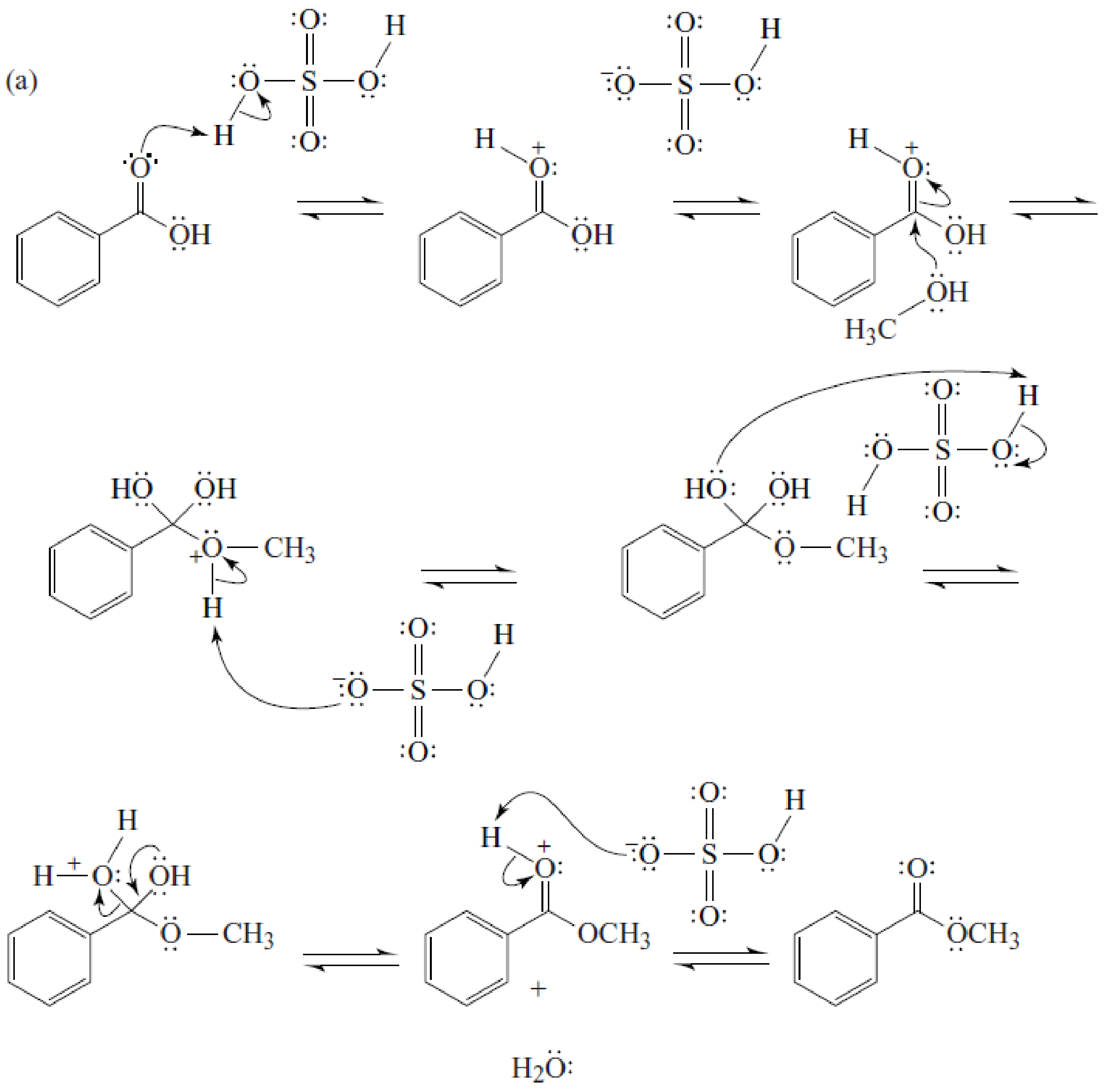
Mechanisms

17.25

See the mechanisms in Section 17.8F, where R = CH_2CH_3 for propanamide.

17.26

(a)



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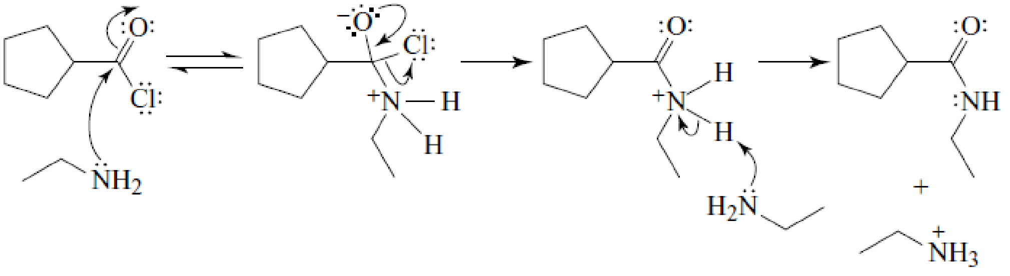
(b)



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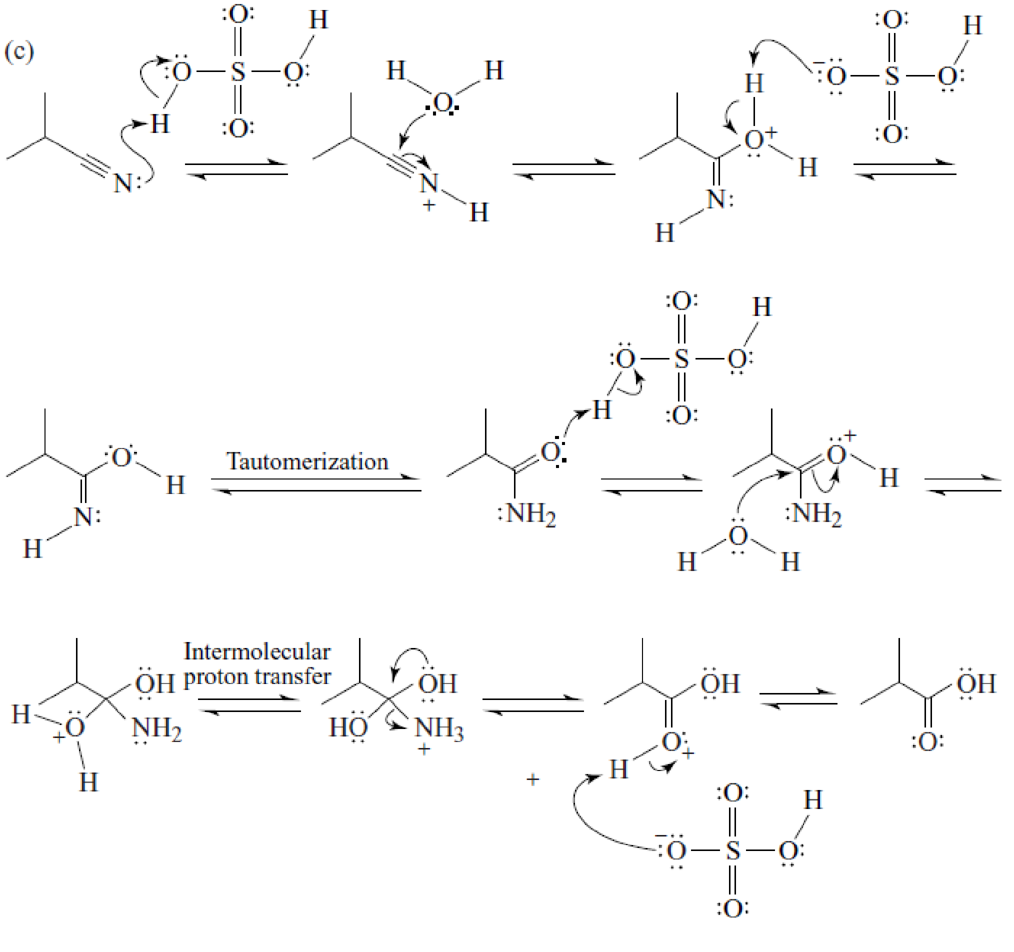

17.27

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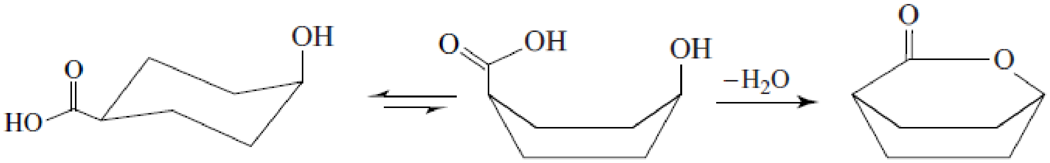
cis-4-Hydroxycyclohexanecarboxylic acid can assume a boat conformation that permits lactone formation.



Neither of the chair conformations nor the boat form of *trans*-4-hydroxycyclohexanecarboxylic acid places the —OH group and the —CO_2H group close enough together to permit lactonization.

Synthesis

17.28

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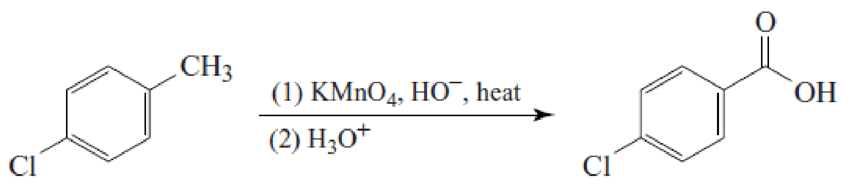
(a)


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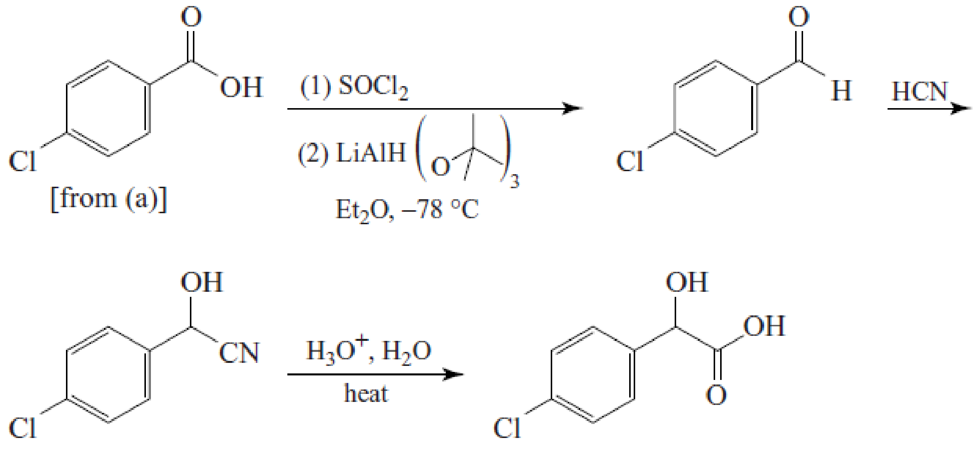

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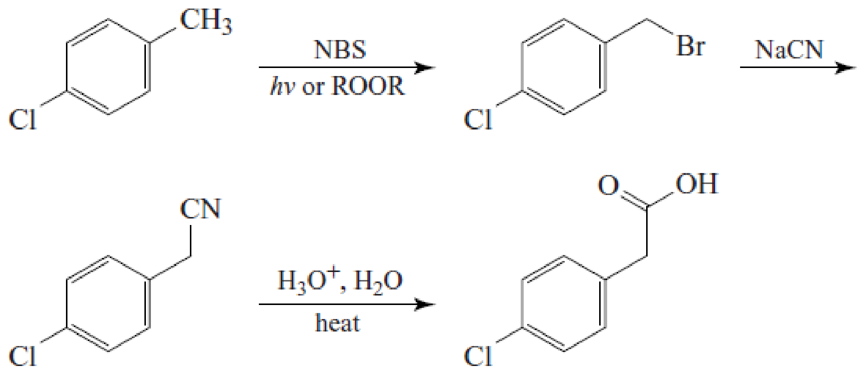

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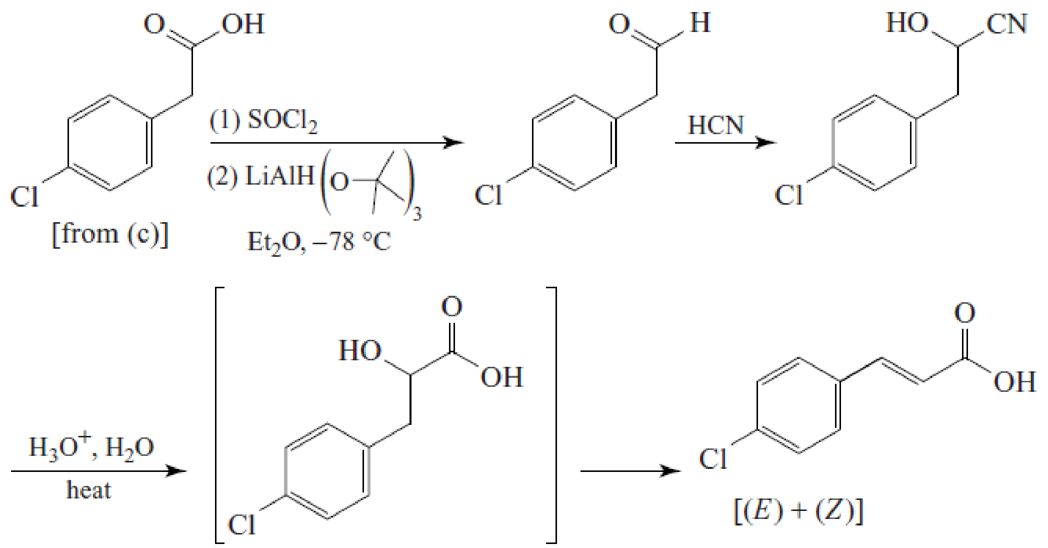

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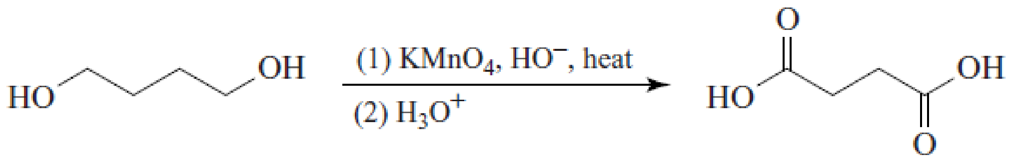
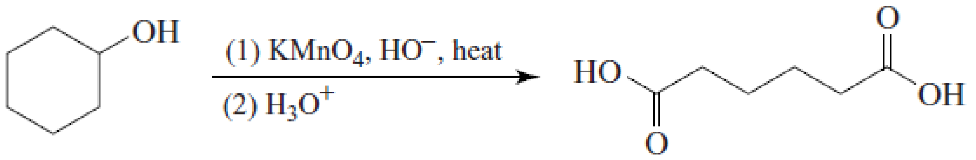
17.29

(a) 

(b) 

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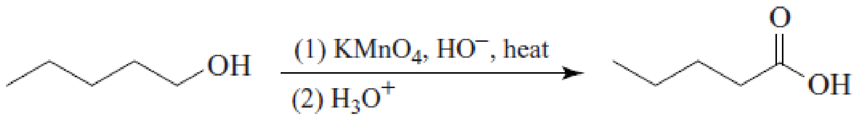
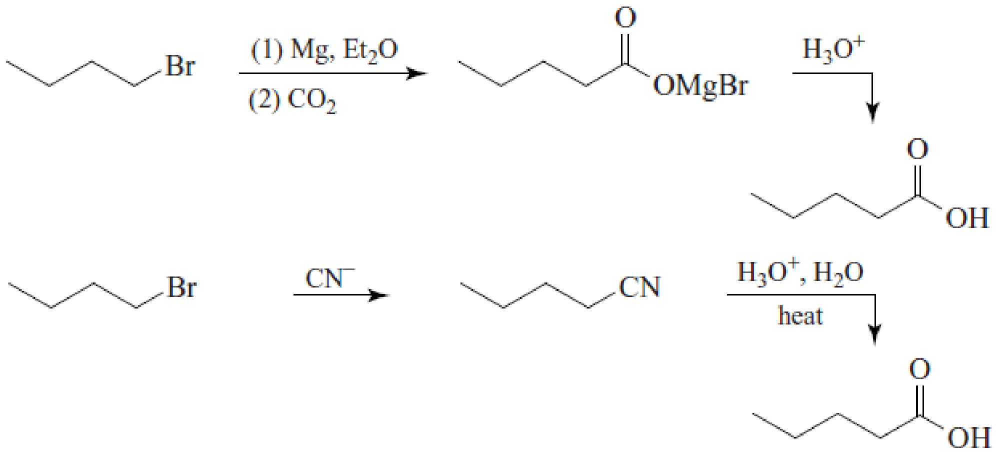
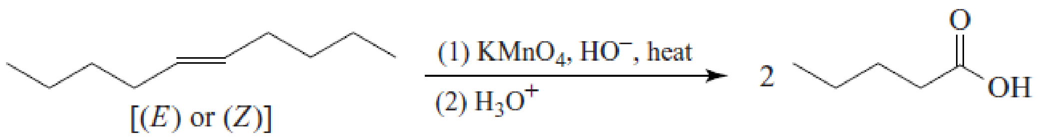
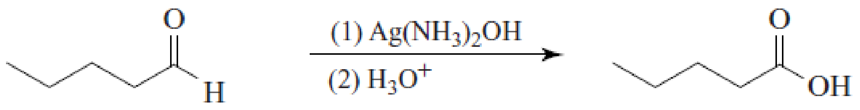
(a) 

(b) 

(c) 

(d) 

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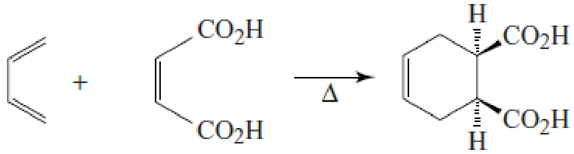
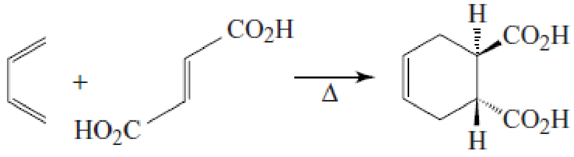
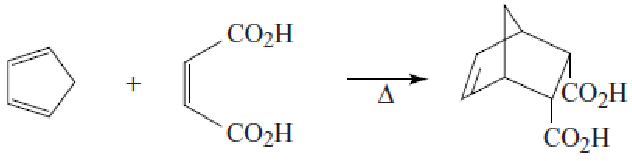
17.32

(a) 

(b) 

(c) 

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<H1> **ADDITIONAL OBJECTIVE QUESTIONS**

<H2> **Single Correct Choice Type**

1. **(d)** The hydroxide ion attacks the C of CN and the negative charge develops on the N atom.
2. **(c)** Ethanol is better nucleophile than water.
3. **(d)** More the electron deficiency on the carbonyl C, more is the rate of reaction.
4. **(d)** Decarboxylation of carboxylic group occurs in the β keto acids formed in a,b,c.
5. **(a)** Decarboxylation of carboxylic group occurs in the β keto acid a.
6. **(c)** A has a Br at o position of methyl, in B nitro is reduced to NH_2, in C amine converted to diazonium, in D, diazonium substituted by H and in E, methyl group oxidized to carboxylic acid.
7. **(b)** More the electron deficiency on the carbonyl C, more is the rate of reaction.
8. **(d)** The C of CO_2 comes from the bicarbonate, which is first converted into carbonic acid and then decomposes to water and CO_2.
9. **(d)** Largest *K*a means strongest acid, d is strongest due to –I effect of three F atoms.
10. (b)
11. **(d)** Decarboxylation of carboxylic group occurs in the β keto acid d.

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12. **(d)** a and b release by decarboxylation, while c releases by acid base reaction followed by decomposition of carbonic acid.
13. **(a)** The C of CO_2 comes from the bicarbonate.
14. **(c)** Decarboxylation occurs to form E and the carboxylic group is released as CO_2 while Iodoform reaction takes place to form F and G with the C^{13} released in iodoform.

15. **(c)** Anhydride formed by attack of carboxylic group on acyl halide.
16. **(a)** More the electron deficiency on the carbonyl C, more is the rate of reaction.
17. **(b)** Decarboxylation takes place, thus two same methyl groups on the former chiral C.
18. (d)

<H2> Linked Comprehension Type

1. (b) Ester is reduced to two alcohols by LAH, of the given choices, only b has 8 C atoms and yields one optically active and one optically inactive product. B is oxidized to butan-2-one (D). D undergoes aldol condensation to yield E. E is reduced to F by Wolff Kishner reduction which reduces the carbonyl to alkane. F undergoes hydroboration-oxidation resulting in addition of OH as per anti-markovnikov on the secondary C atom to form G. G is then oxidized to ketone.
2. (b)
3. (b)
4. (b)
5. (c) Only in option c, the product of hydrolysis followed by dehydration produces geometrical isomers. The molecule B is formed by hydrolysis of A into a carboxylic acid and alcohol group. D is formed by the oxidation of alcohol group of B. E id formed by decarboxylation of the β keto acid D.
6. (c)
7. (c)
8. (b)

<H2> Matrix Match Type

1. (a)→(p, s); (b)→(q, s); (c)→(p, s); (d)→(r)

In geminal dicarboxylic acid (two carboxylic groups on the same carbon), one carboxylic group undergoes decarboxylation and is replaced by H.

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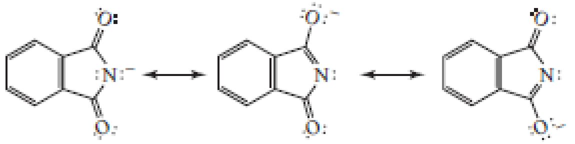
Chapter 18: Amines

Practice Problems

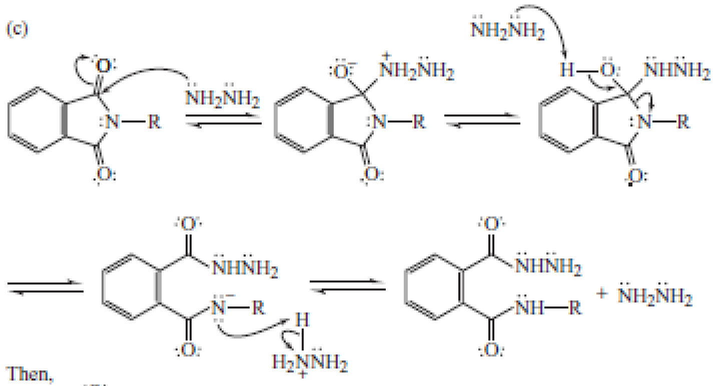
18.1

(a) Neglecting Kekulé forms of the ring, we can write the following resonance structures for the phthalimide anion.

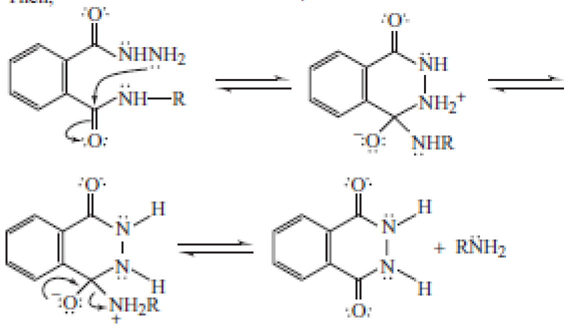


(b) Phthalimide is more acidic than benzamide because its anion is stabilized by resonance to a greater extent than the anion of benzamide. (Benzamide has only one carbonyl group attached to the nitrogen atom, and thus fewer resonance contributors are possible.)

(c)



Then,



18.2

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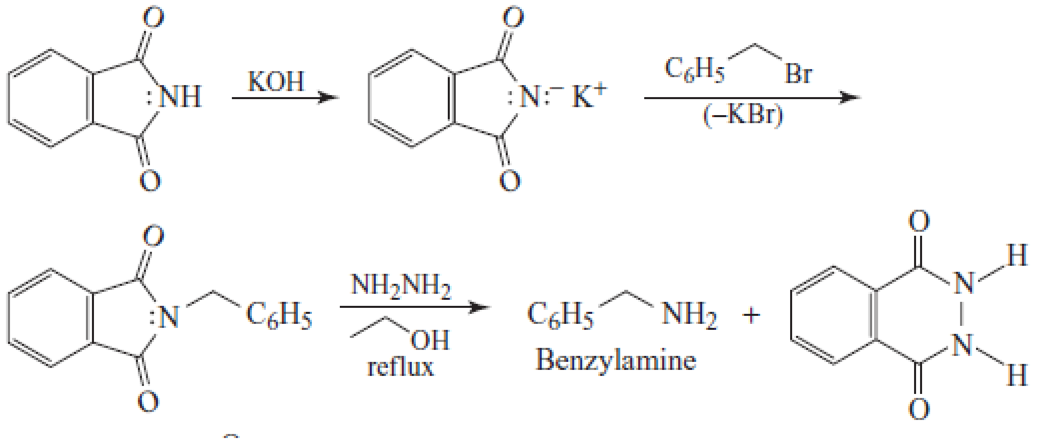
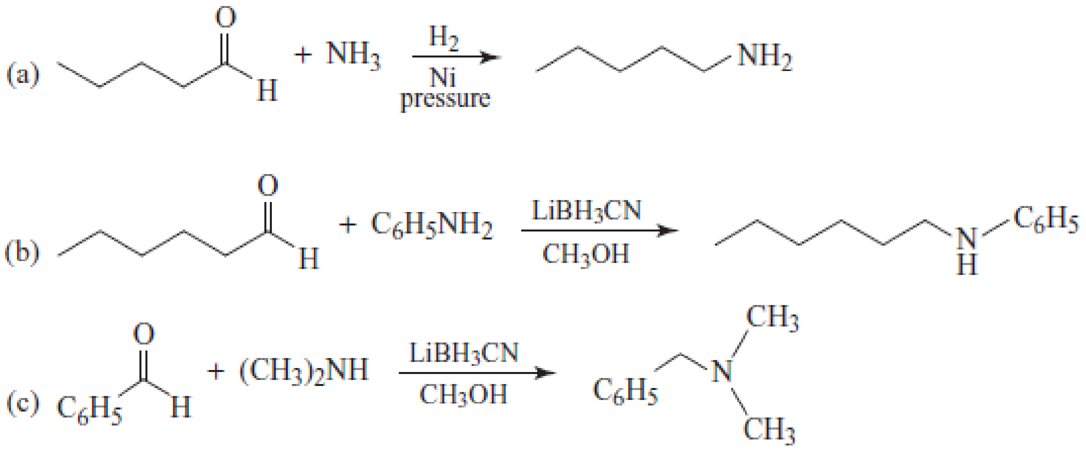


18.3



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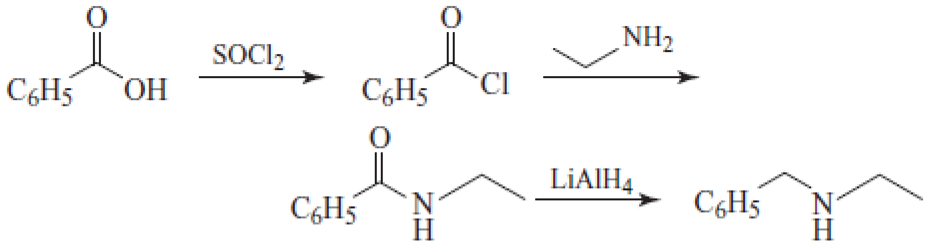
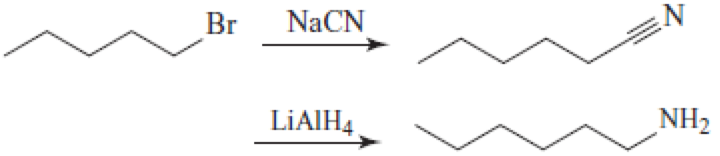
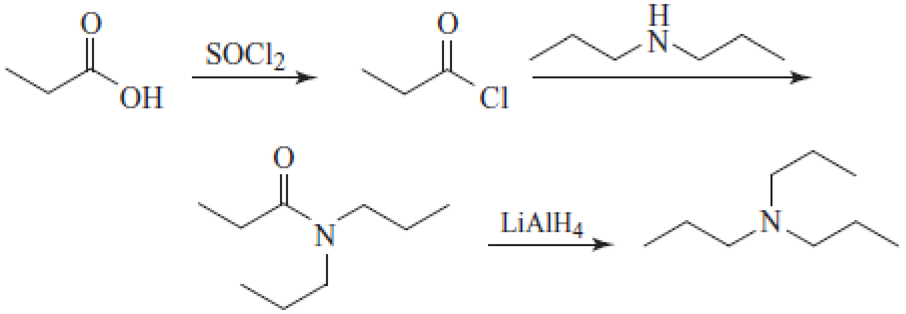
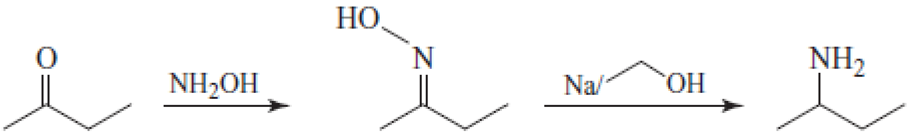
(a) 

(b) 

(c) 

(d) 

18.5

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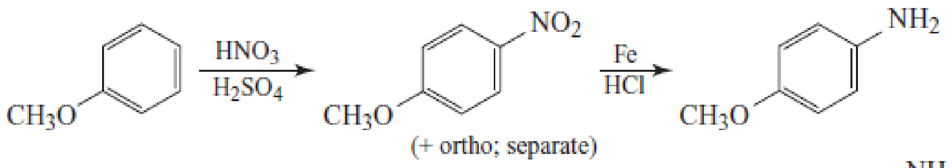

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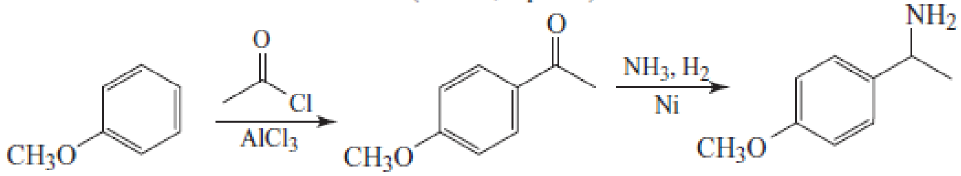

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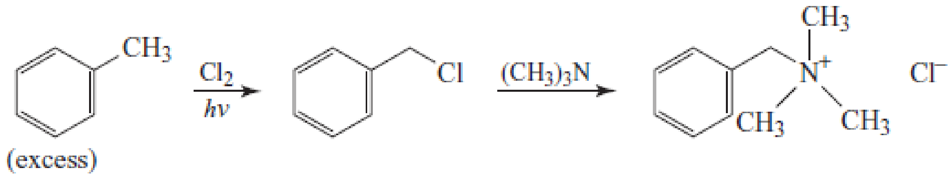

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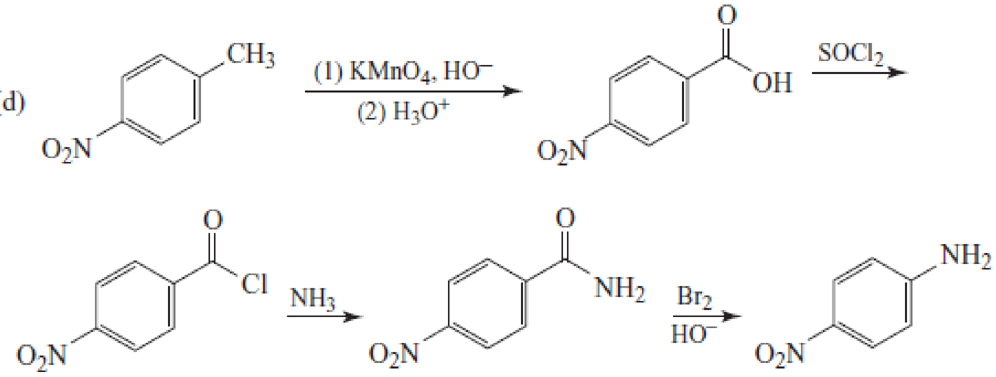

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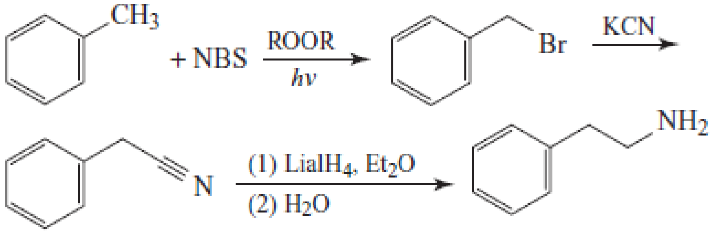

18.6

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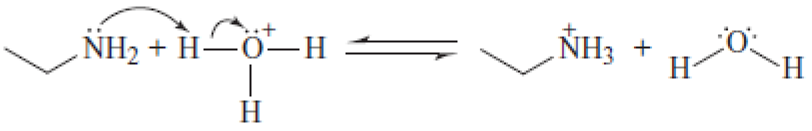
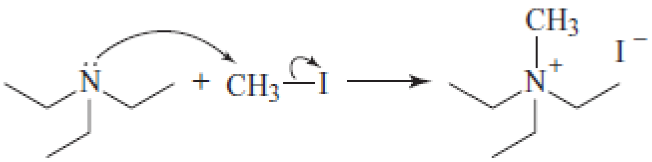
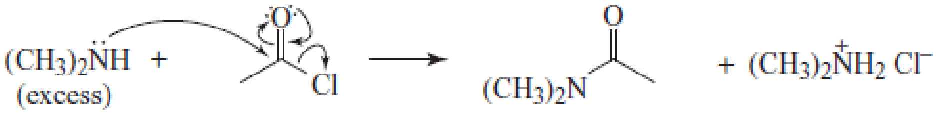
An amine acting as a base.



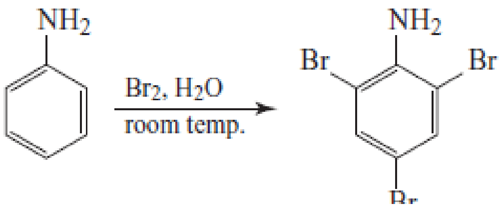
An amine acting as a nucleophile in an alkylation reaction.



An amine acting as a nucleophile in an acylation reaction.



An amino group acting as an activating group and as an ortho-para director in electrophilic aromatic substitution.



18.7

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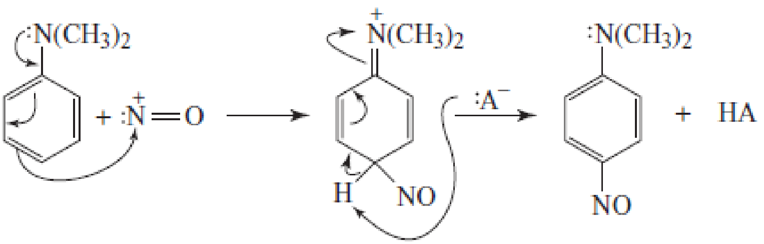
(a, b) $^{-}O—\ddot{N}=O + H_3O^+ \rightleftharpoons HO—\ddot{N}=O + H_2O$

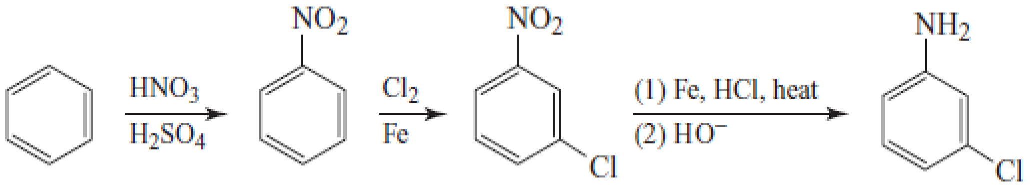
$$HO—\ddot{N}=O + H_3O^+ \rightleftharpoons H\overset{+}{O}(H)—\ddot{N}=O + H_2O$$

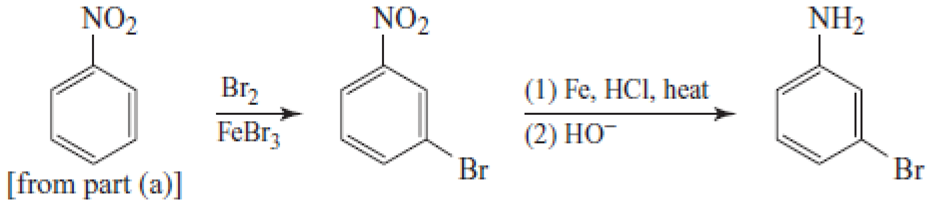
$$H\overset{+}{O}(H)—\ddot{N}=O \rightleftharpoons H_2O + :\overset{+}{N}=O$$



(c) The $\overset{+}{N}O$ ion is a weak electrophile. For it to react with an aromatic ring, the ring must have a powerful activating group such as $-OH$ or $-NR_2$.

18.8

(a) 

(b) 

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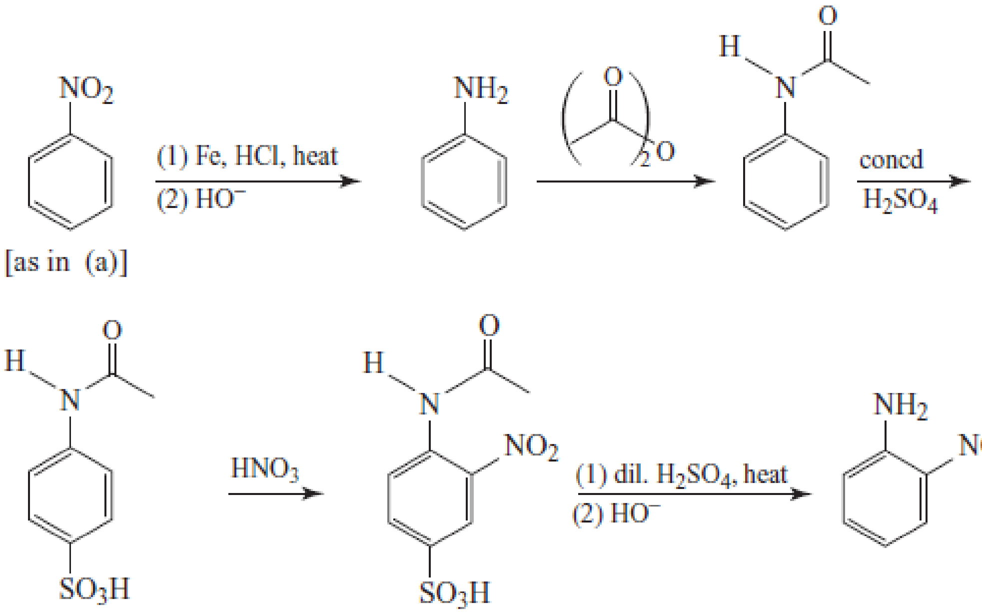
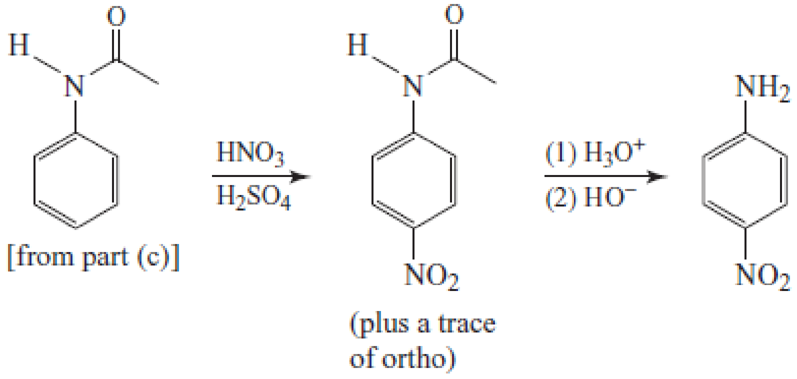
(c) 

(d) 

18.9

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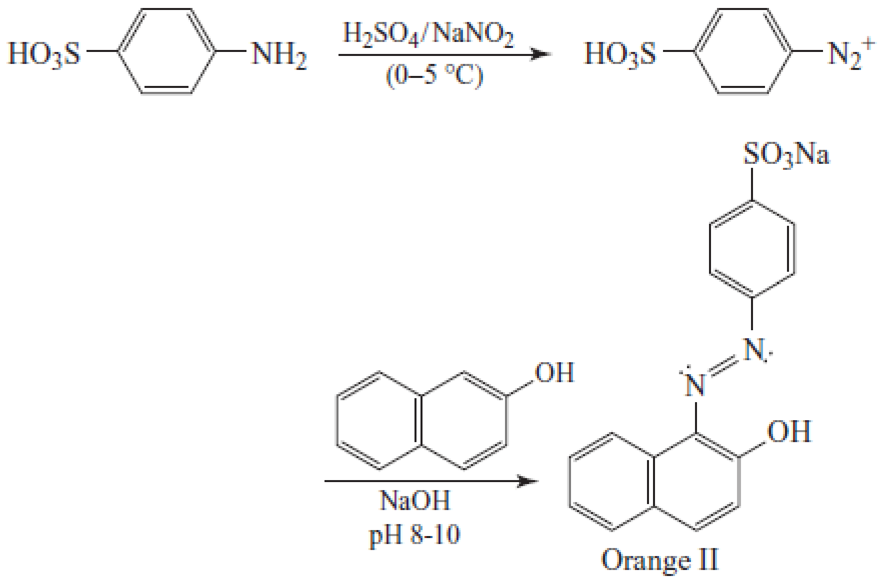

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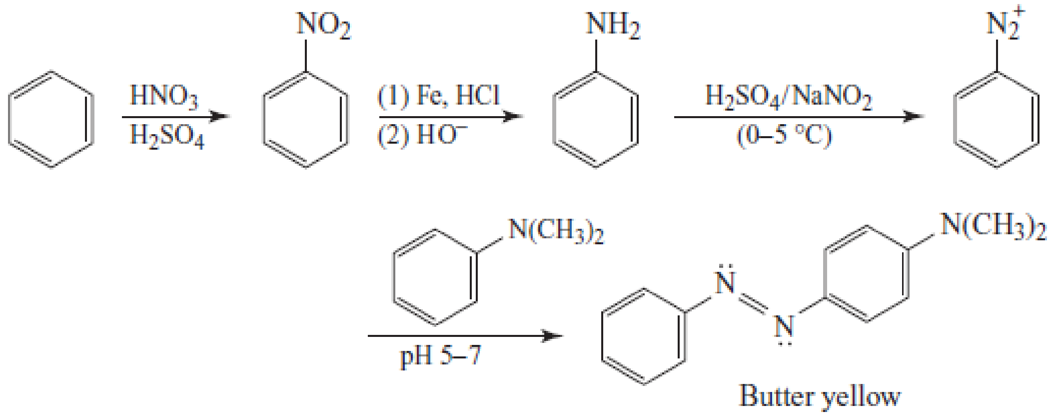

18.11

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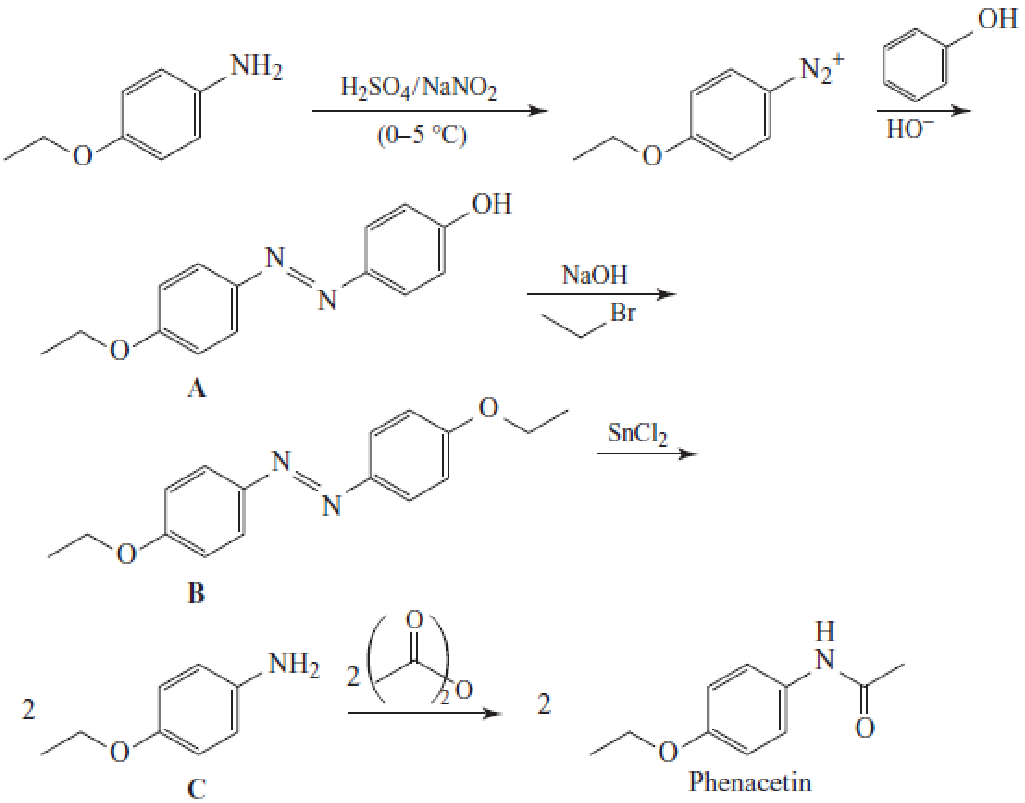
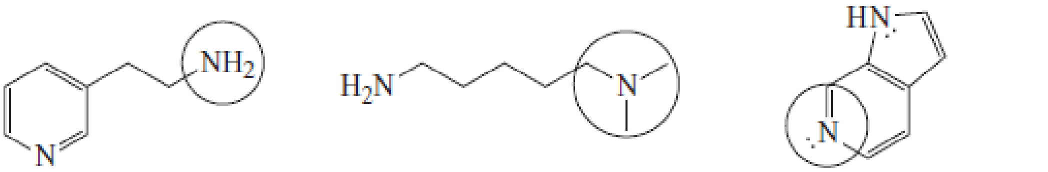


Review Problems

Amine Synthesis and Reactivity

18.12



*sp*³ hybridization stabilizes the corresponding conjugate acid.

Alkyl groups are electron donating, stabilizing the corresponding conjugate acid.

Lone pair is not involved in aromaticity.

18.13

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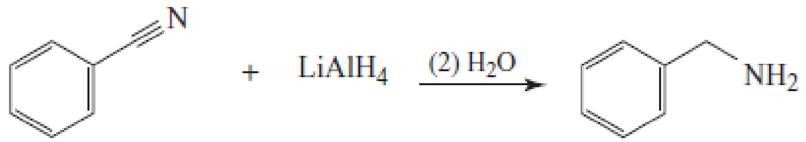
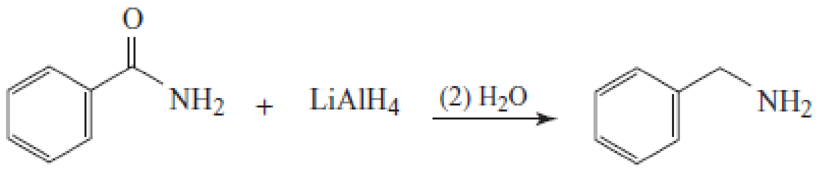
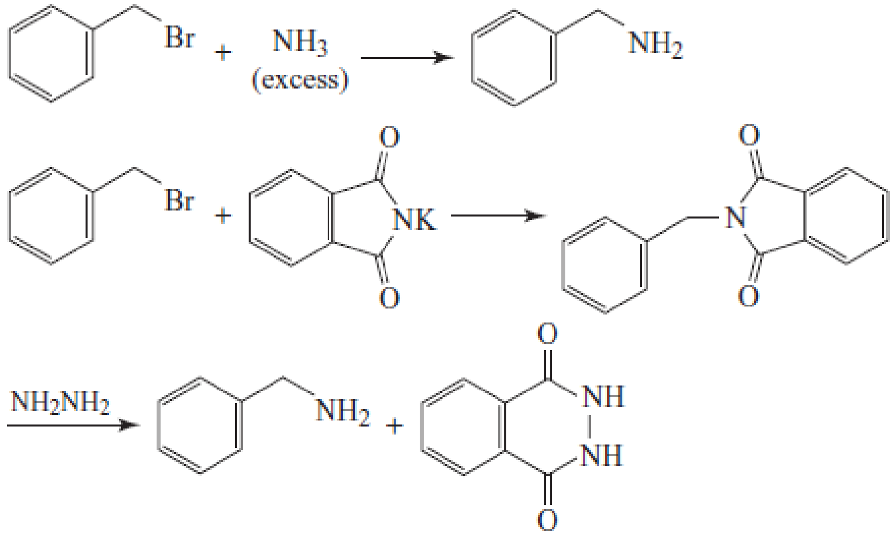
(a) 

(b) 

(c) 

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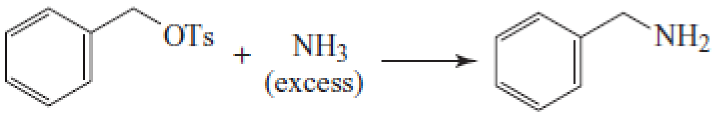
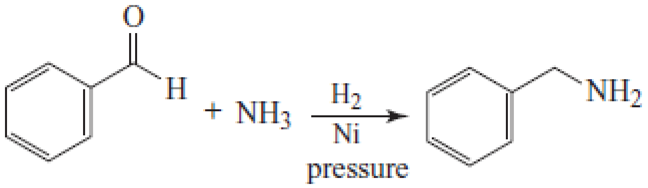
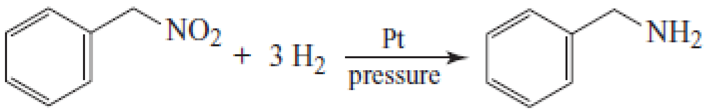
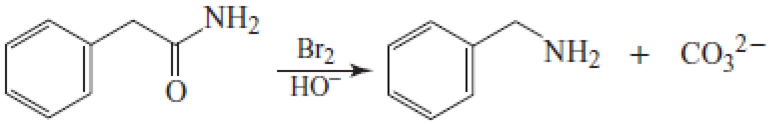
(d) 

(e) 

(f) 

(g) 

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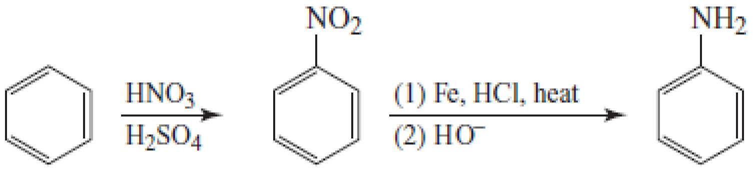
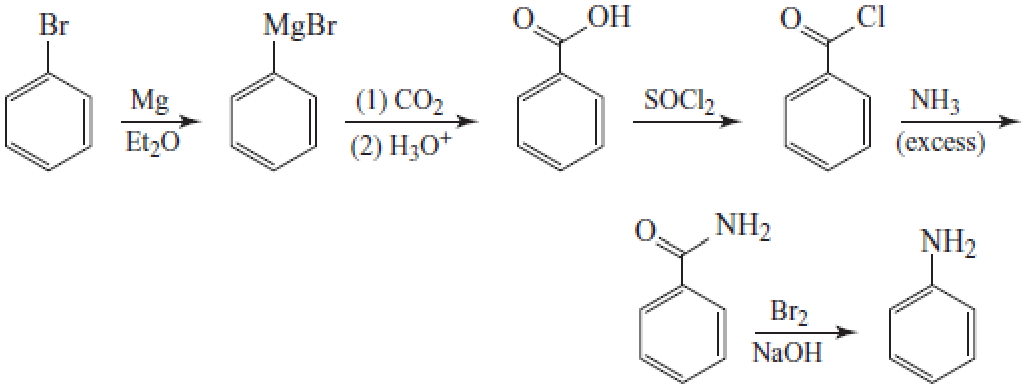
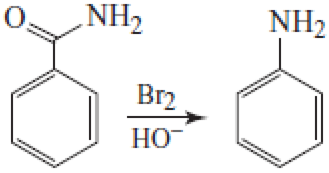
(a) 

(b) 

Hofmann rearrangement

(c) 

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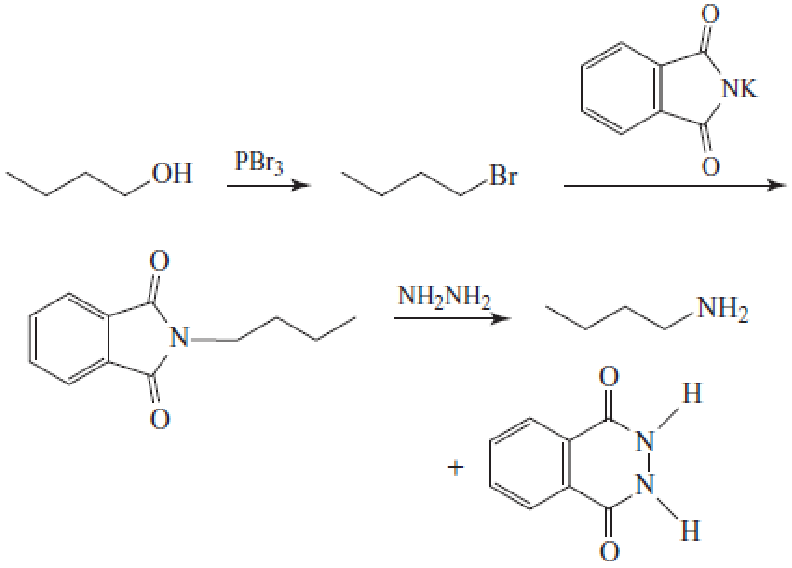
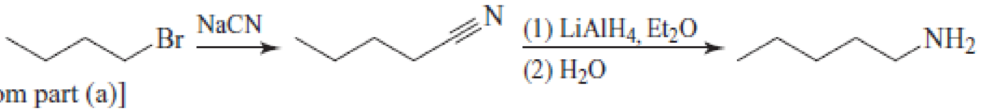
18.15

(a) 

(b) 

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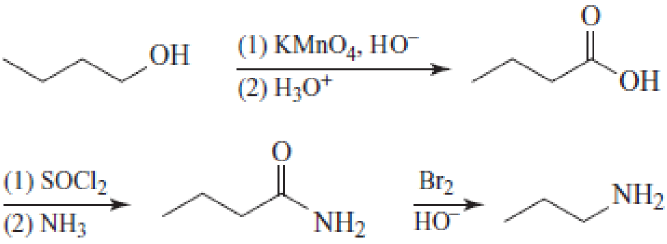
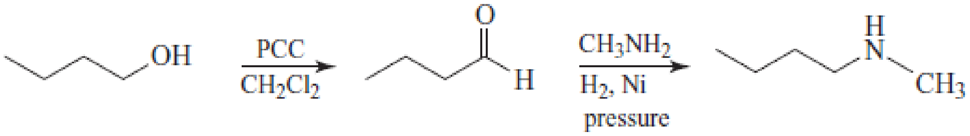
(c) 

(d) 

18.16

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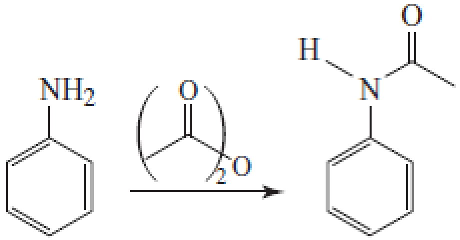
5 (a)



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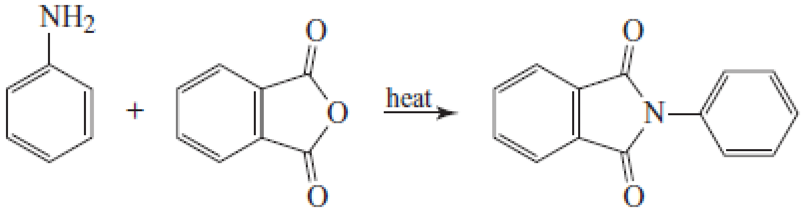

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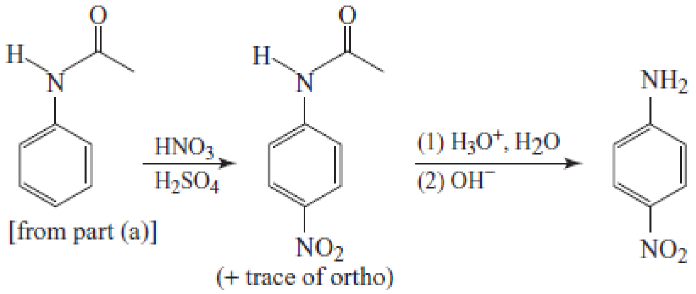
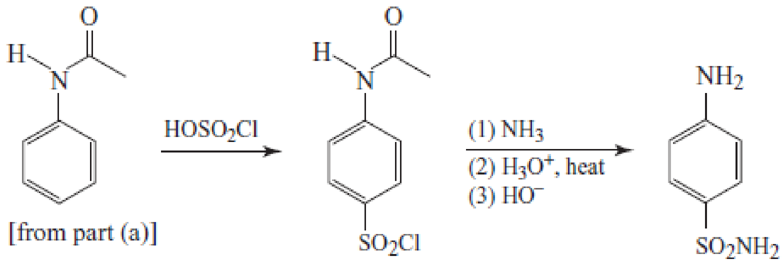
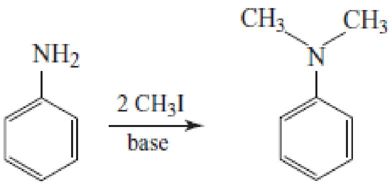
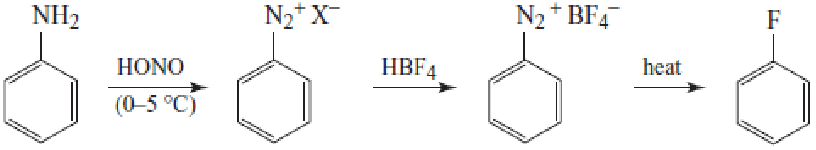
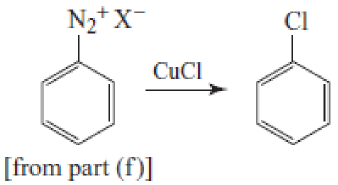
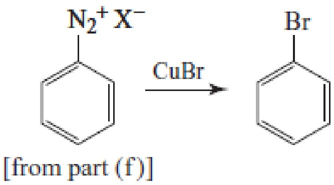
(c) 

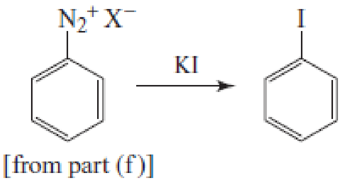
(d) 

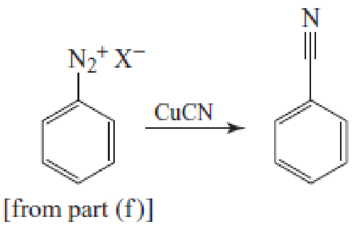
(e) 

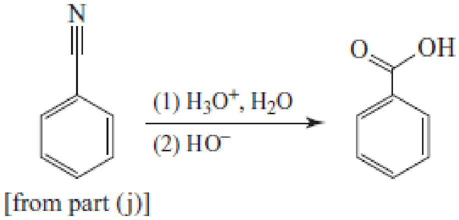
(f) 

(g) 

(h) 

(i) 

(j) 

(k) 

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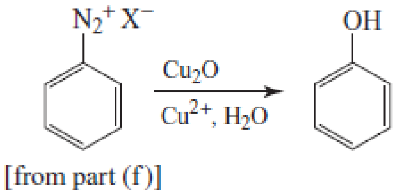

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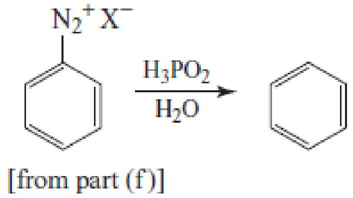

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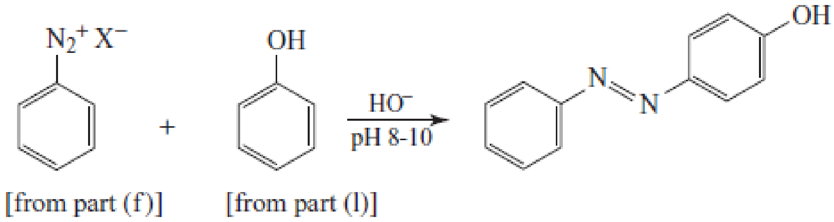

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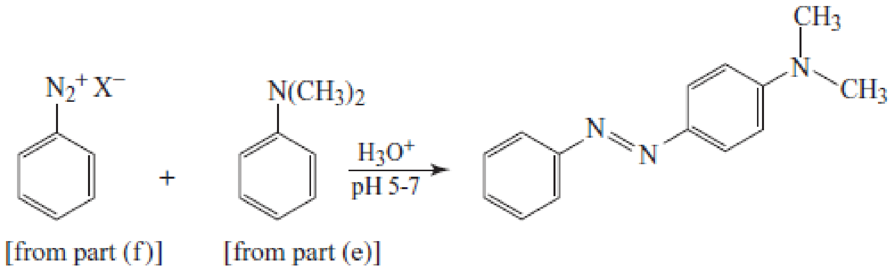

18.17

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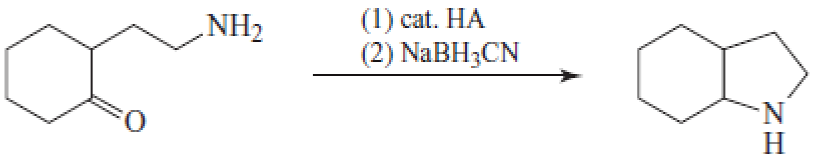
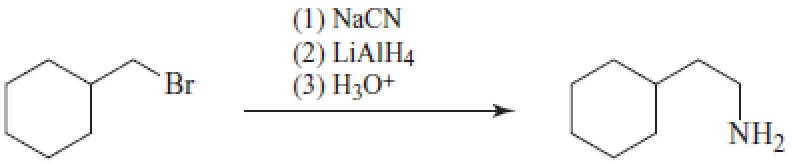
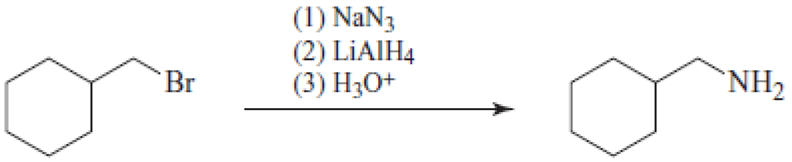
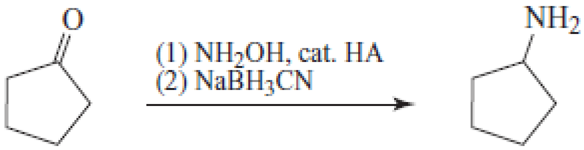
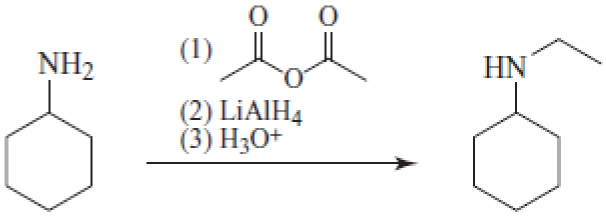
(a) 

(b) 

(c) 

(d) 

(e) 

18.18

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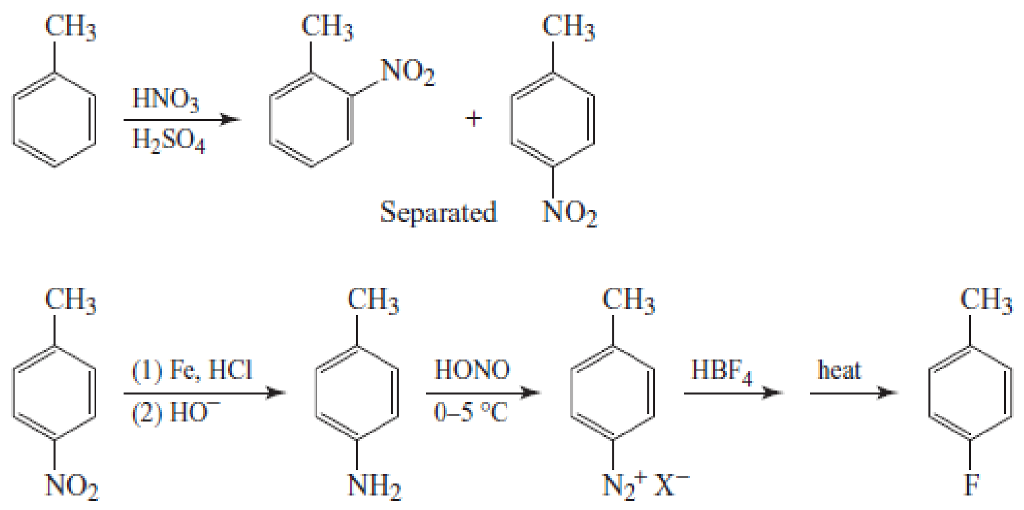

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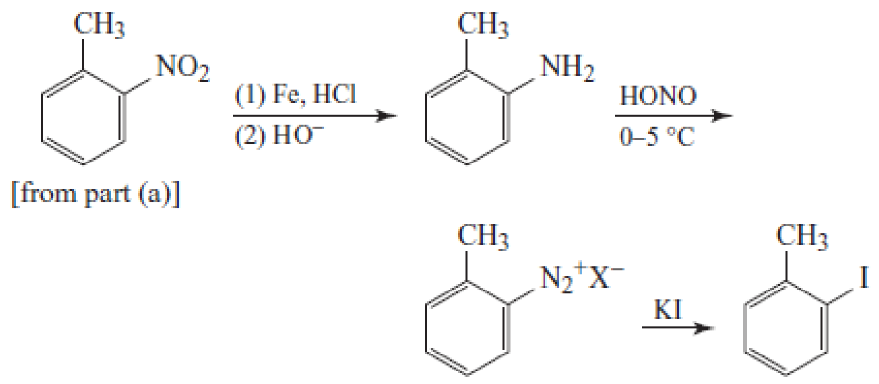

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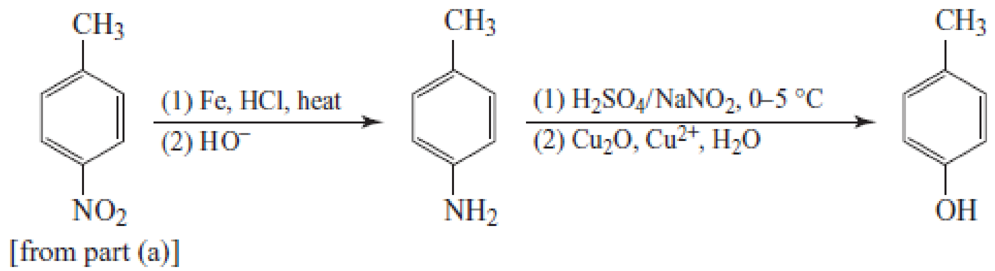

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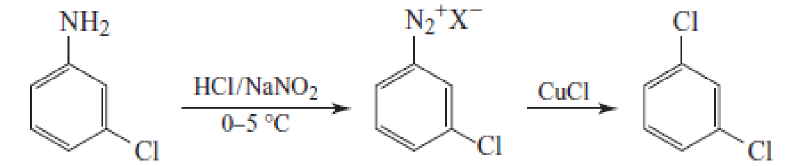
(d) 

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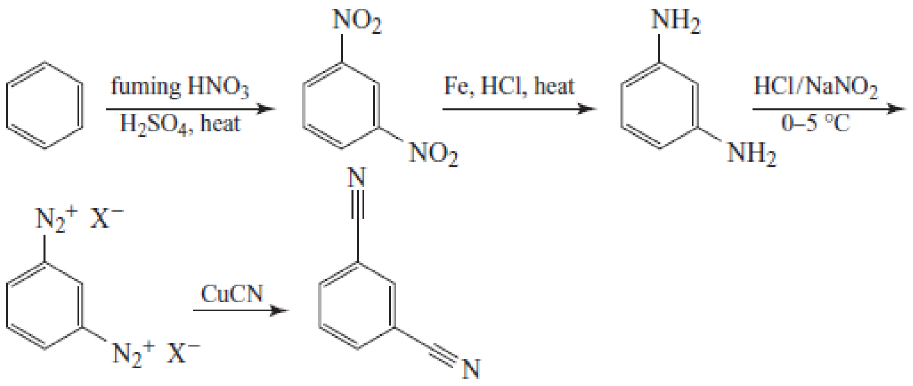
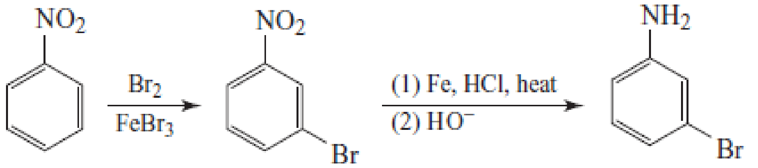
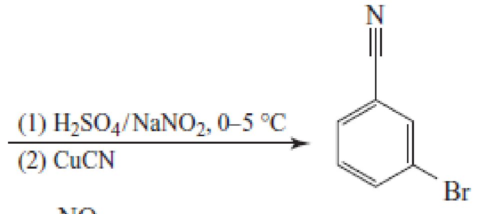
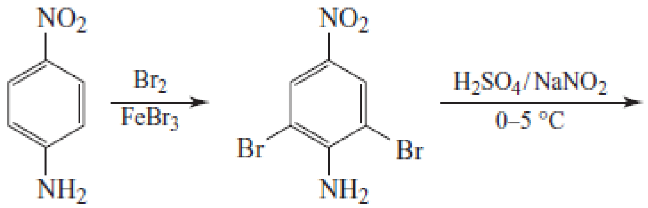
(e) 

(f) 

[from Problem 20.10(a)]



(g) 

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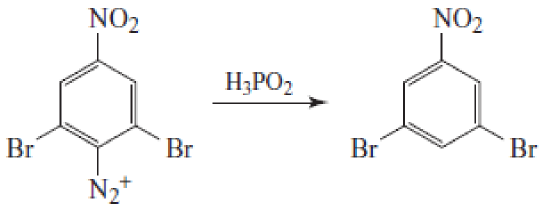
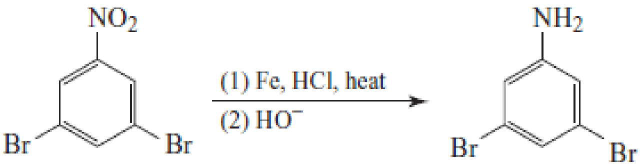


(h) 

[from part (g)]

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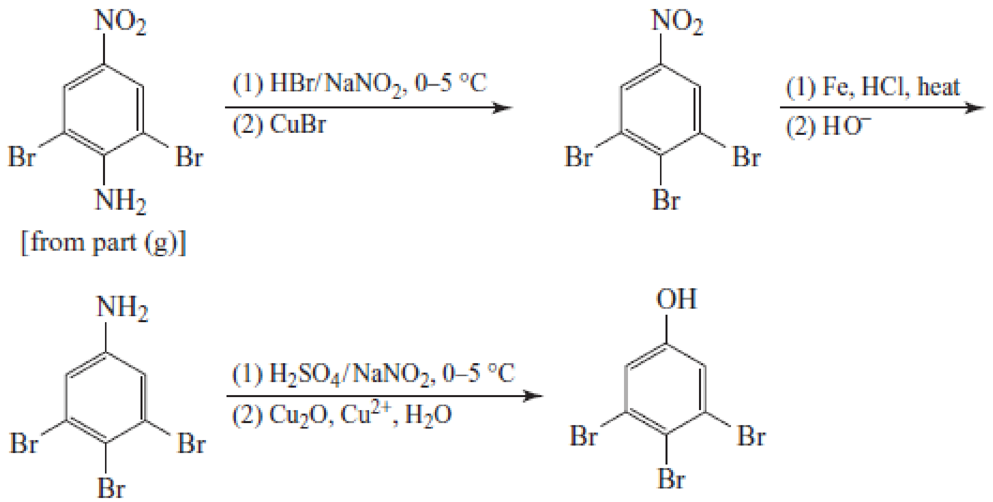

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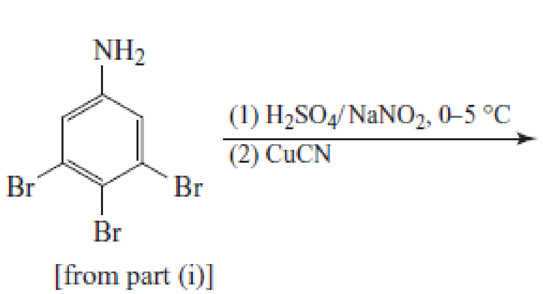

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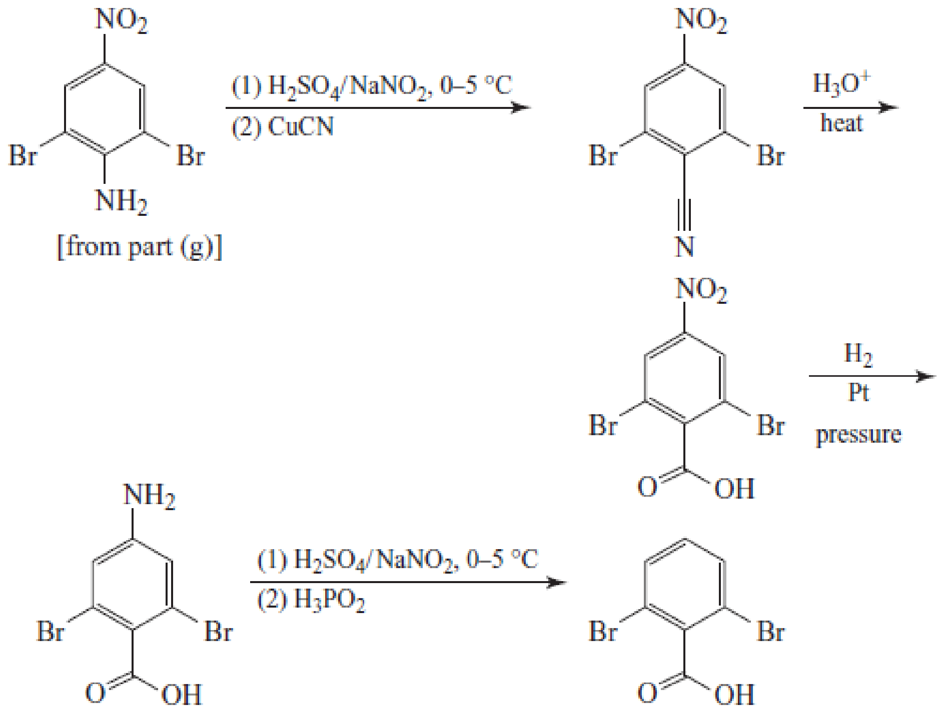

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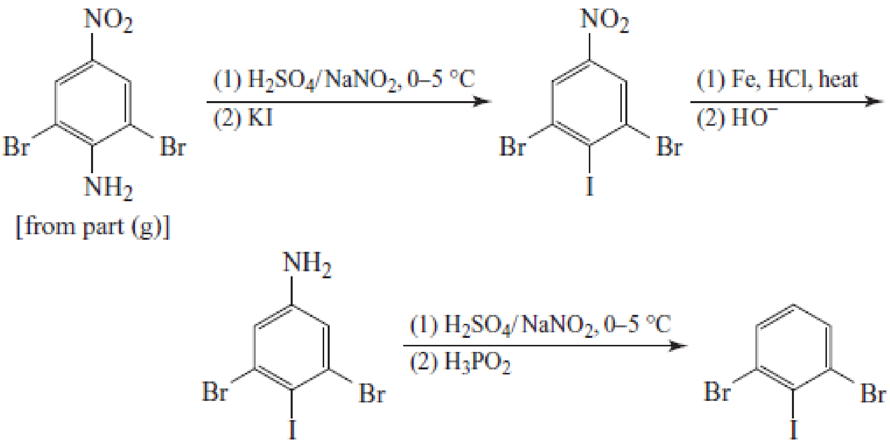

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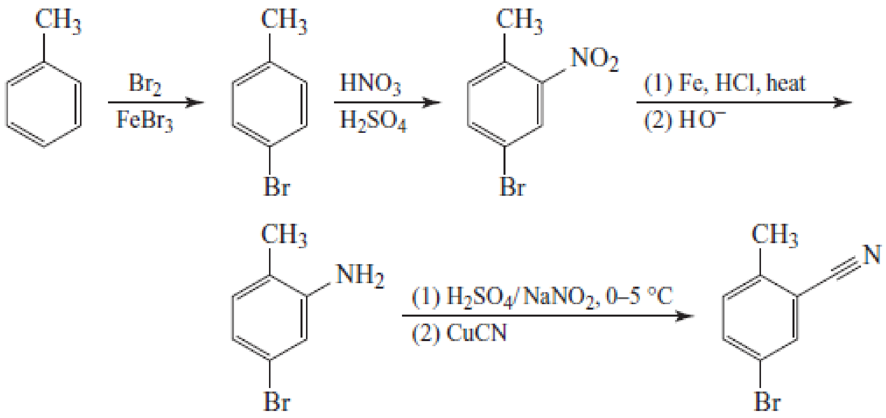

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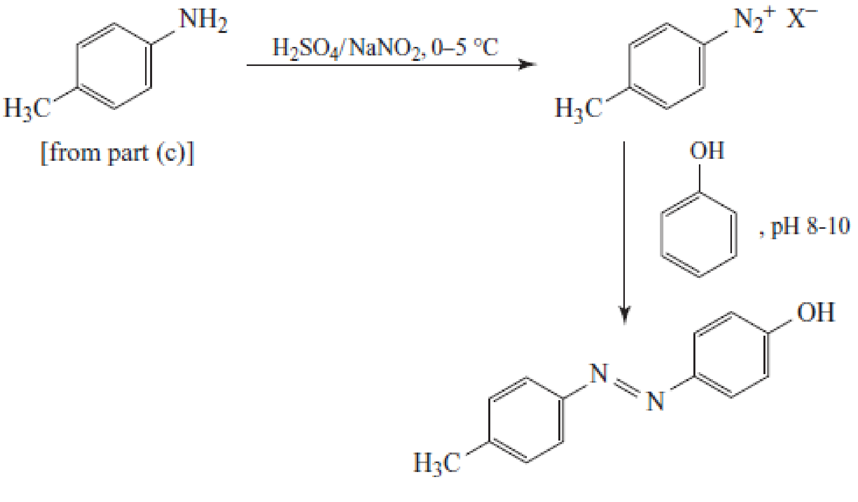

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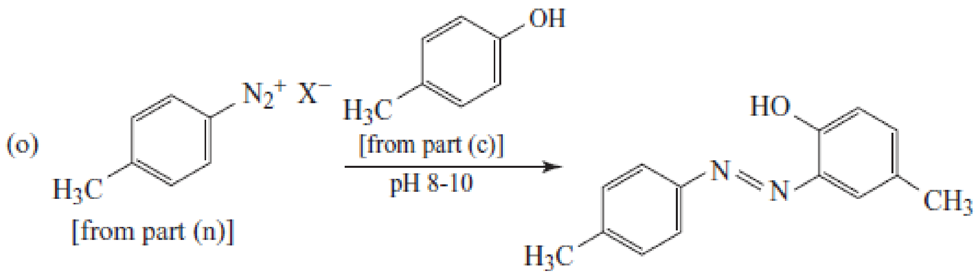

18.19

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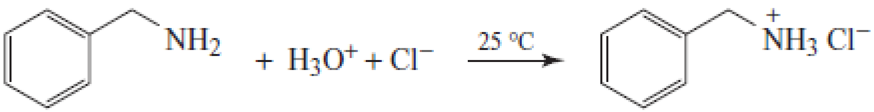
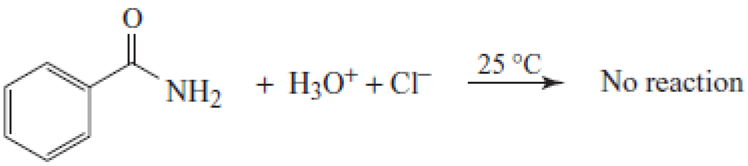
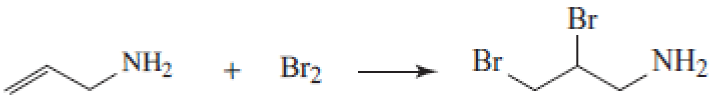
(a) Benzylamine dissolves in dilute HCl at room temperature,



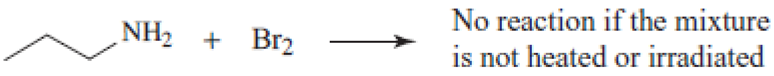
benzamide does not dissolve:



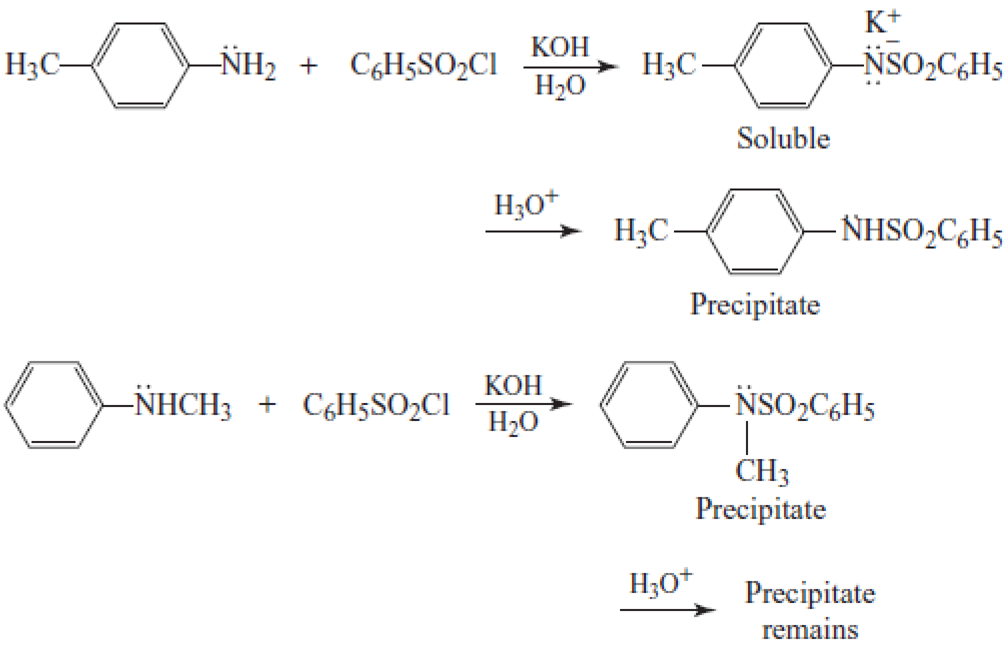
(b) Allylamine reacts with (and decolorizes) bromine instantly,



propylamine does not:



(c) The Hinsberg test:



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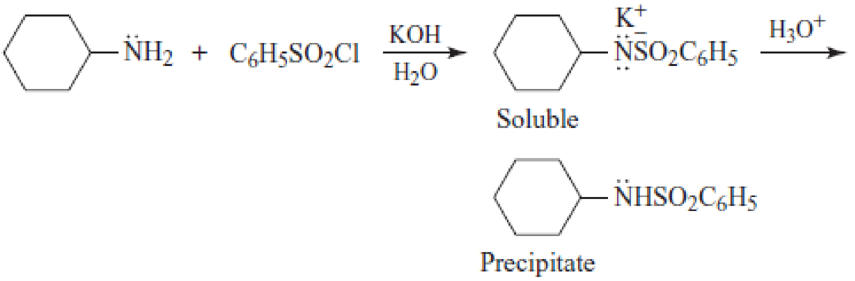
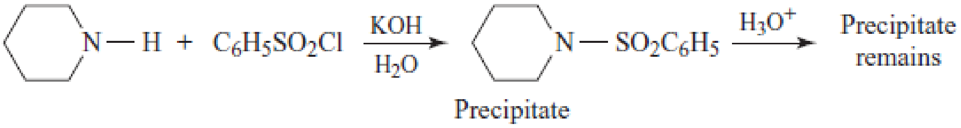
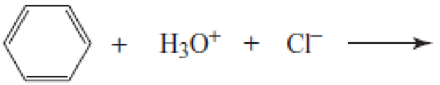
(d) The Hinsberg test:



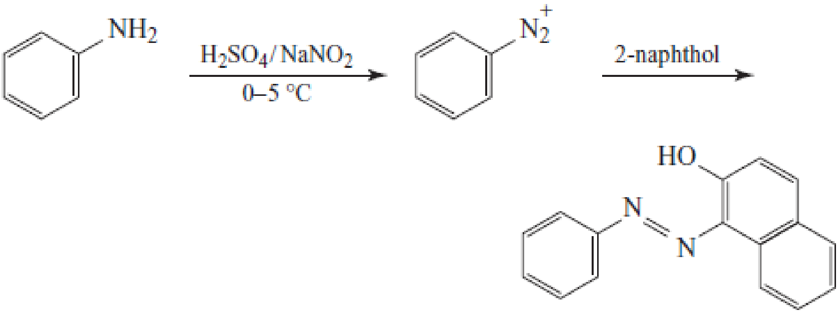


(e) Pyridine dissolves in dilute HCl,

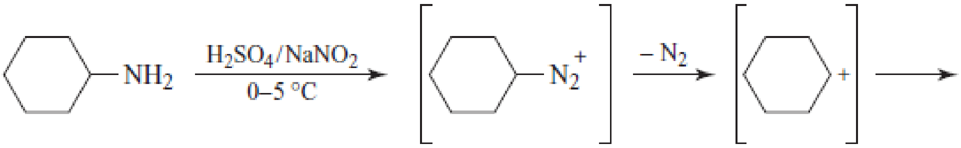
benzene does not:



(f) Aniline reacts with nitrous acid at 0–5 °C to give a stable diazonium salt that couples with 2-naphthol, yielding an intensely colored azo compound.



Cyclohexylamine reacts with nitrous acid at 0–5 °C to yield a highly unstable diazonium salt—one that decomposes so rapidly that the addition of 2-naphthol gives no azo compound.



alkenes, alcohols, and alkyl halides $\xrightarrow{\text{2-naphthol}}$ No reaction

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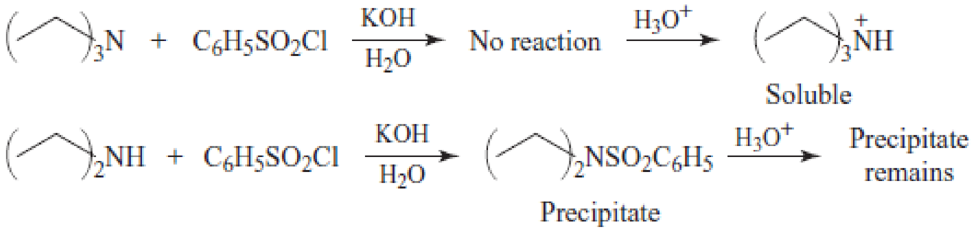
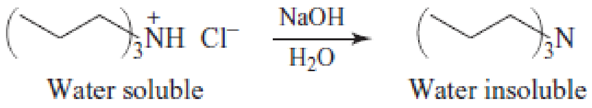
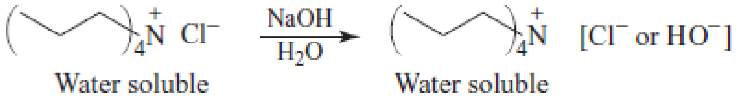
(g) The Hinsberg test:



(h) Tripropylaminium chloride reacts with aqueous NaOH to give a water insoluble tertiary amine.



Tetrapropylammonium chloride does not react with aqueous NaOH (at room temperature), and the tetrapropylammonium ion remains in solution.



(i) Tetrapropylammonium chloride dissolves in water to give a neutral solution. Tetrapropylammonium hydroxide dissolves in water to give a strongly basic solution.

Mechanisms

18.20

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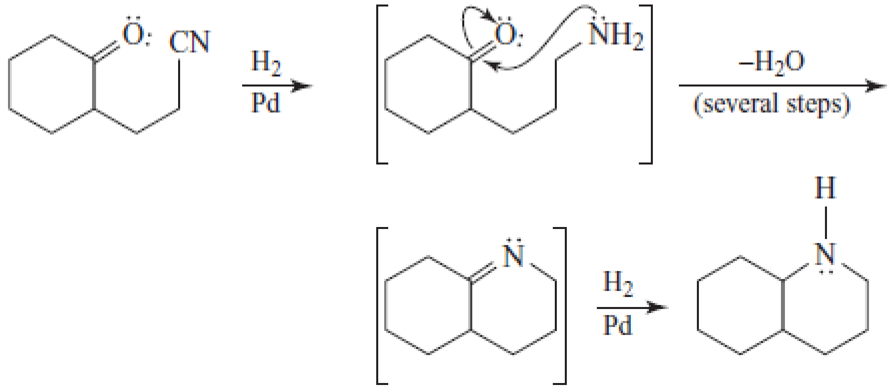

18.21

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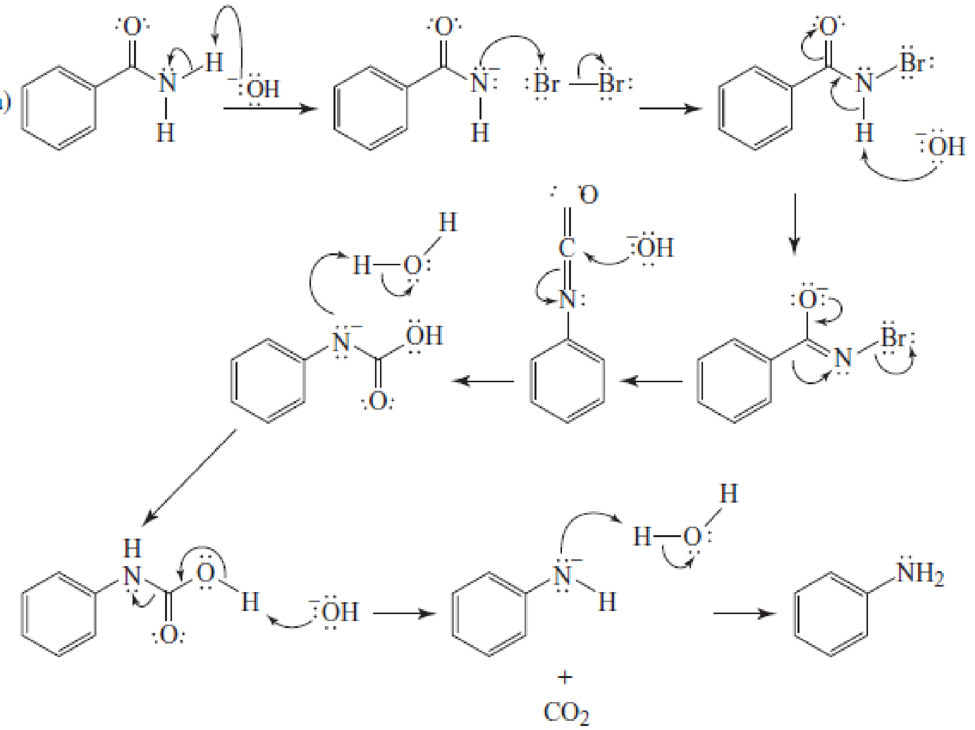
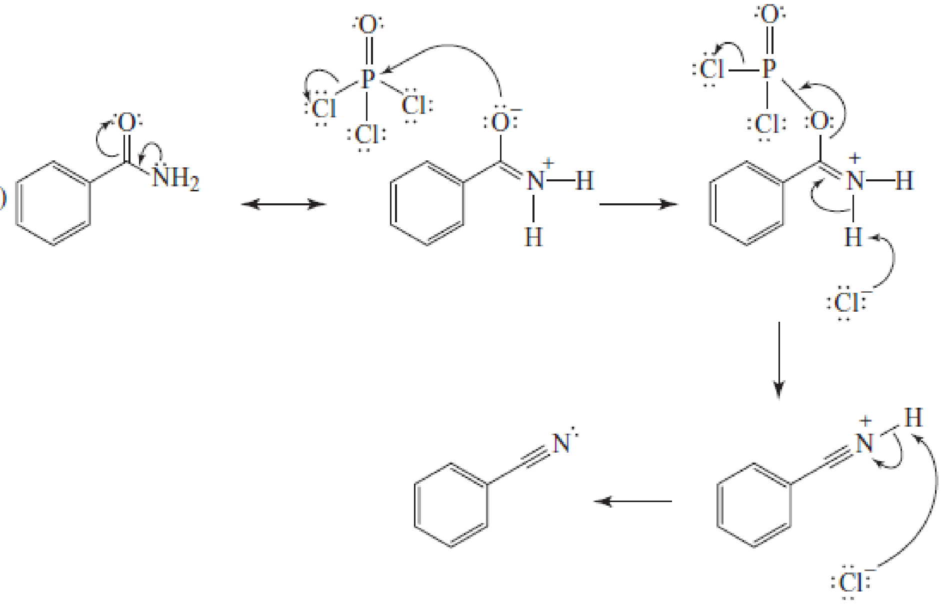
(a)



(b)



18.22

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Carry out the Hofmann reaction using a mixture of ^{15}N labeled benzamide, $C_6H_5CO^*NH_2$, and *p*-chlorobenzamide. If the process is intramolecular, only labeled aniline, $C_6H_5{}^*NH_2$, and *p*-chloroaniline, will be produced.

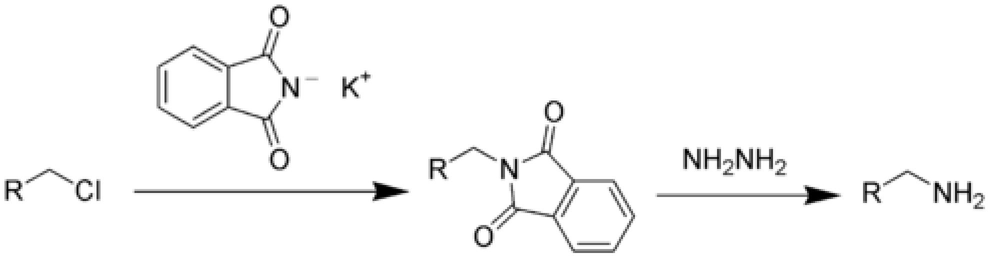
If the process is one in which the migrating moiety truly separates from the remainder of the molecule, then, in addition to the two products mentioned above, there should be produced both the unlabeled aniline and labeled *p*-chloroaniline, *p*-$ClC_6H_4{}^*NH_2$.

Note: When this experiment is actually carried out, analysis of the reaction mixture by mass spectrometry shows that the process is intramolecular.

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (b) It is Hofmann Bromamide reaction.



2. **(b)**

3. **(c)** Gabriel Synthesis is shown in Q.2.
4. **(b)** A is formed by Friedel Crafts alkylation, iso-propyl is introduced at para position to N on left ring. Amide undergoes hydrolysis to yield aniline derivative. In C, the amine group is converted to diazonium salt which then undergoes azo coupling to form D (option b).

5. (c) Bromination occurs at para position in first step which then undergoes SNAr.

6. **(c)** A is diazonium salt and B is formed by azo coupling at para position to the activating OH group.

7. **(a)** B is Ammonium propanoate while C is propanamide which undergoes Hofmann rearrangement to form ethanamine.
8. **(a)** A is diazonium salt, B is 4-methylphenol while C is formed by Riemer Tiemann reaction.
9. (**b)** The dye is orange coloured.
10. **(c)** Carbocation will form at the position of amine from diazonium, followed by migration of isopropyl group due to formation of more stable carbocation.

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11. **(c)** Wurtz reaction is to form longer chain alkane from smaller alkyl halides.
12. **(a)** Formation of diazonium at the position of amine, followed by hydride shift and formation of ketone.
13.**(a)** Formation of diazonium in A followed by its substitution with F.
14. **(d)** Formation of carbocation at the position of diazonium salt, followed by ring expansion.
15. **(a)** Aliphatic diazonium salt are unstable.
16.**(d)** The given compound is used as a dye.
17. **(a)** In basic medium, phenol converts to phenoxide with strong +M of oxide group, thus azo coupling takes place with respect to the OH group.
18. (c) Secondary amine gives nitroso.

19. **(a)** Formation of diazonium followed by substitution with OH.
20. **(a)** Secondary amine gives nitroso.
21. **(c)** Primary aromatic amine gives the reaction.
22. **(b)** It requires greater number of elimination as it has the least number of methyl groups attached to amine in the reactant.
23. (a) Diazonium salt will be product.
24. **(d)** Guanidine is a strong base as the conjugate acid is resonance stabilized.
25.**(a)** A is formed by nitration at ortho position to N, B is formed by hydrolysis of amide to amine, C has a diazonium group at the position of amine which is then substituted by H.
26.(**c)** Lesser the electron withdrawing effect, lesser is the rate of SNAr.
27. (d)
28. **(b)** The electrophilic aromatic substitution will take place at o/p position with respect to the activating group N.

<H2> Integer Type

1. **(5)** Here, x=3 and y=2.

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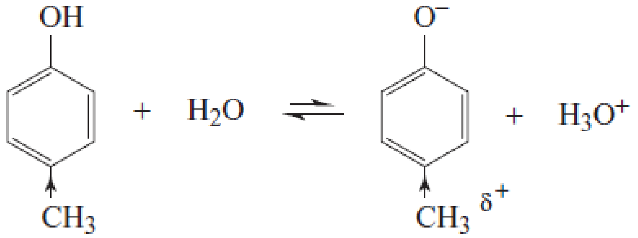
Chapter 19: Phenols and Aryl Halides

Practice Problems

19.1

The inductive effect of an electron-releasing group (i.e., $-CH_3$) changes the charge distribution in the molecule so as to increase the electron density of the ring and oxygen, causing the proton to be held more strongly; it also destabilizes the phenoxide anion by intensifying its negative charge. These effects make the substituted phenol less acidic than phenol itself.



Electron-releasing $-CH_3$ destabilizes the anion more than the acid. pK_a is larger than for phenol.

19.2

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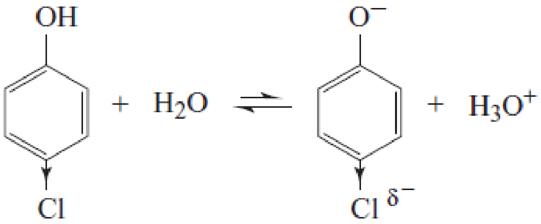
The inductive effect of an electron-withdrawing group such as chlorine changes the charge distribution in the molecule so as to decrease the electron density of the ring and oxygen, causing the proton to be held less strongly; it also can stabilize the phenoxide ion by dispersing its negative charge. These effects make the substituted phenol more acidic than phenol itself.



Electron-withdrawing chlorine stabilizes the anion by dispersing the negative charge. pK_a is smaller than for phenol.

Nitro groups are very powerful electron-withdrawing groups by their inductive and resonance effects. Resonance structures (**B–D**) below place a positive charge on the hydroxyl

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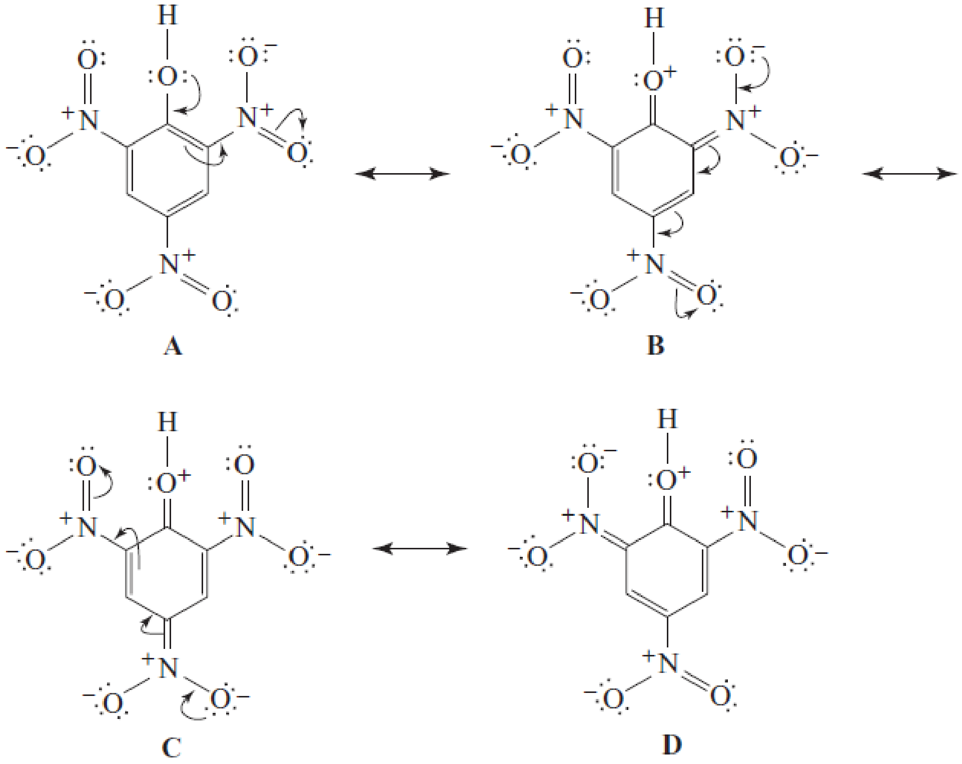
oxygen. This effect makes the hydroxyl oxygen dramatically more positive, causing the proton to be held much less strongly. These contributions explain why 2,4,6-trinitrophenol (picric acid) is so exceptionally acidic.



19.3

Dissolve the mixture in a solvent such as CH_2Cl_2 (one that is immiscible with water). Using a separatory funnel, extract this solution with an aqueous solution of sodium bicarbonate. This extraction will remove the benzoic acid from the CH_2Cl_2 solution and transfer it (as sodium benzoate) to the aqueous bicarbonate solution. Acidification of this aqueous extract will cause benzoic acid to precipitate; it can then be separated by filtration and purified by recrystallization.

The CH_2Cl_2 solution can now be extracted with an aqueous solution of sodium hydroxide. This will remove the 4-methylphenol (as its sodium salt). Acidification of the aqueous extract will cause the formation of 4-methylphenol as a water-insoluble layer. The 4-methylphenol can then be extracted into ether, the ether removed, and the 4-methylphenol purified by distillation.

The CH_2Cl_2 solution will now contain only toluene (and CH_2Cl_2). These can be separated easily by fractional distillation.

19.4

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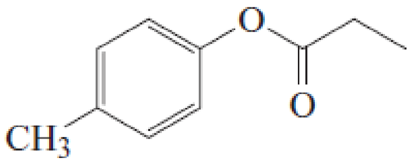
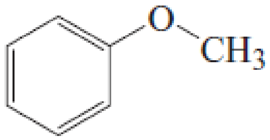
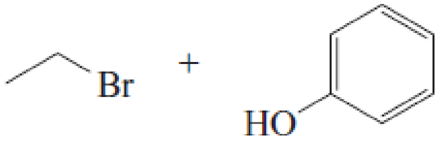
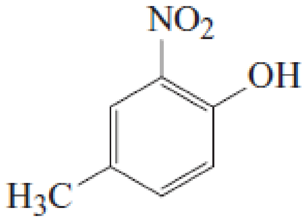
(a) 

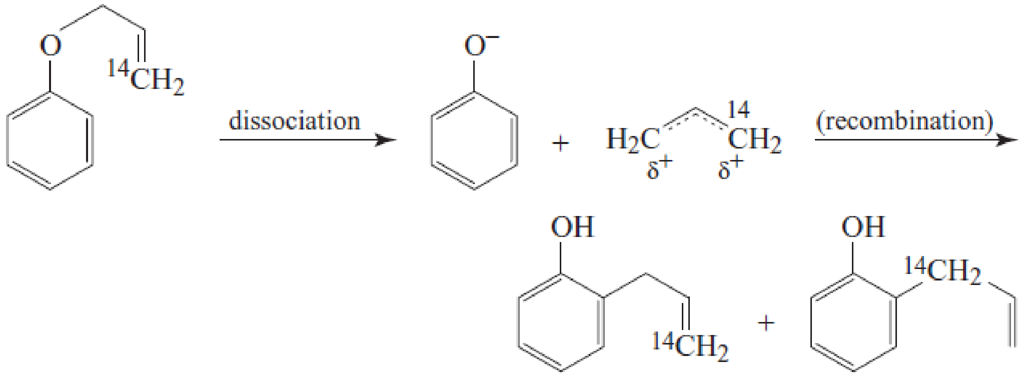
(b) 

(c) 

(d) 

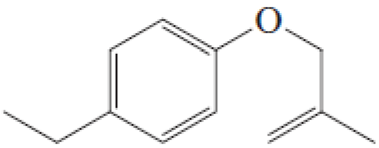
19.5

If the mechanism involved dissociation into an allyl cation and a phenoxide ion, then recombination would lead to two products: one in which the labeled carbon atom is bonded to the ring and one in which an unlabeled carbon atom is bonded to the ring.

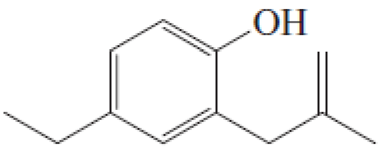


The fact that all of the product has the labeled carbon atom bonded to the ring eliminates this mechanism from consideration.

19.6



A



B

19.7

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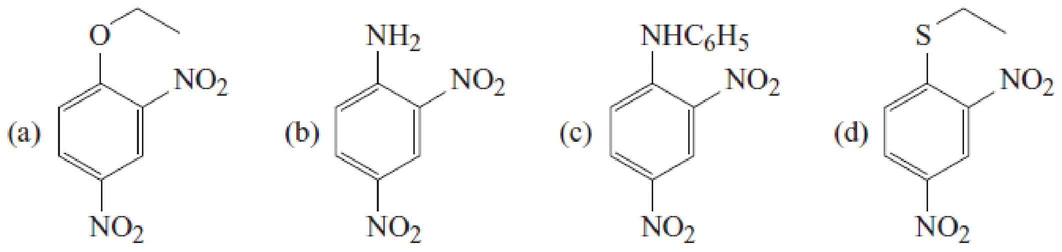
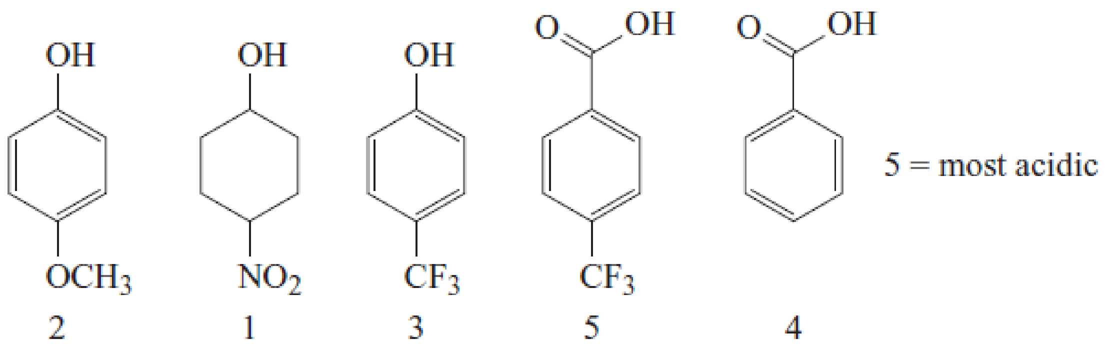


Review Problems

Physical Properties

19.8

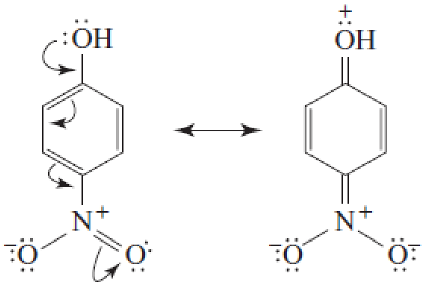


19.9

(a) 4-Fluorophenol because fluorine is an electron withdrawing group and a methyl is an electron donating group.

(b) 4-Nitrophenol because a nitro group is electron withdrawing and a methyl is an electron donating group.

(c) 4-Nitrophenol because the nitro group can exert an electron-withdrawing effect through resonance.

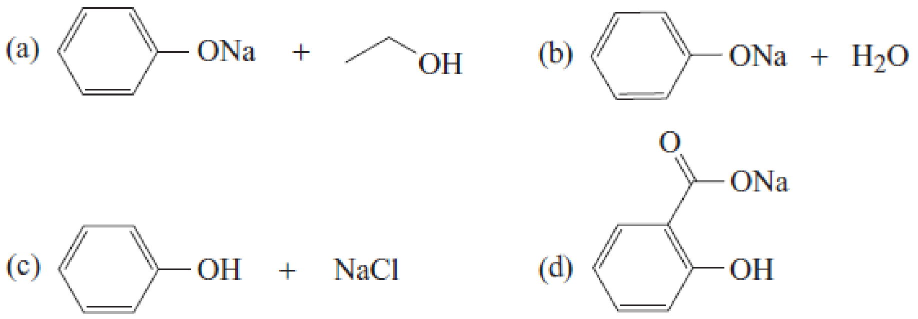


In 3-nitrophenol these resonance structures are not possible.

(d) 4-Methylphenol because it is a phenol, not an alcohol.

(e) 4-Fluorophenol because fluorine is more electronegative than bromine.

19.10



19.11

(a) 4-Chlorophenol will dissolve in aqueous NaOH; 4-chloro-1-methylbenzene will not.

(b) 4-Methylbenzoic acid will dissolve in aqueous $NaHCO_3$; 4-methylphenol will not.

(c) 2,4,6-Trinitrophenol, because it is so exceptionally acidic ($pK_a = 0.38$), will dissolve in aqueous $NaHCO_3$; 4-methylphenol ($pK_a = 10.17$) will not.

(d) 4-Ethylphenol will dissolve in aqueous NaOH; ethyl phenyl ether will not.

General Reactions

19.12

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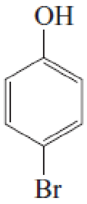
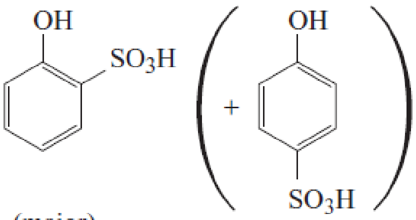
(a) 

(major)

(b) 

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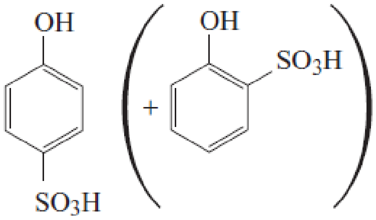
(c) 

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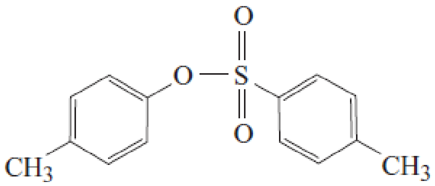
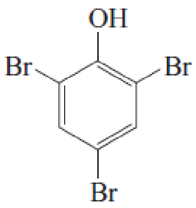
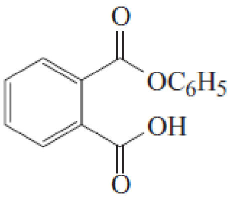
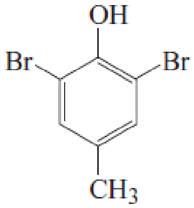
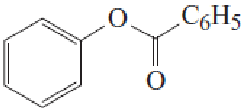
(d) 

(e) 

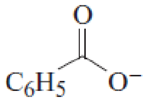
(f) 

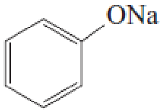
(g) 

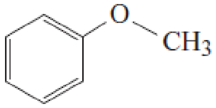
(h) 

(i) Same as (h)

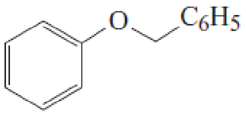
+



(j) 

(k)  + $CH_3OSO_2O^-$

(l) $C_6H_5OCH_3$

(m) 

19.13

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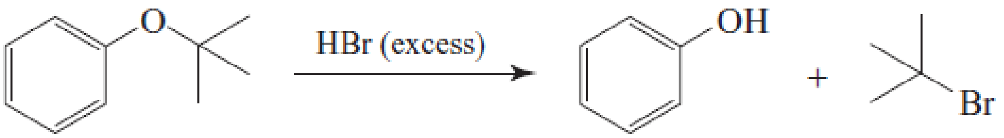
(a) 

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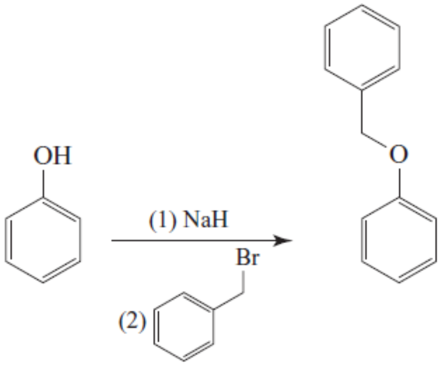
(b)



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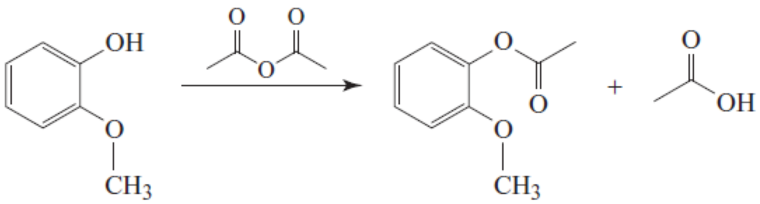

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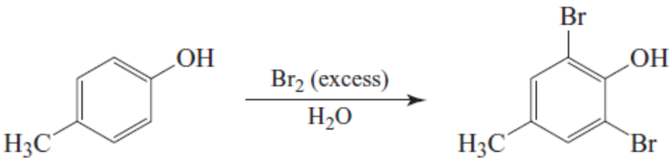

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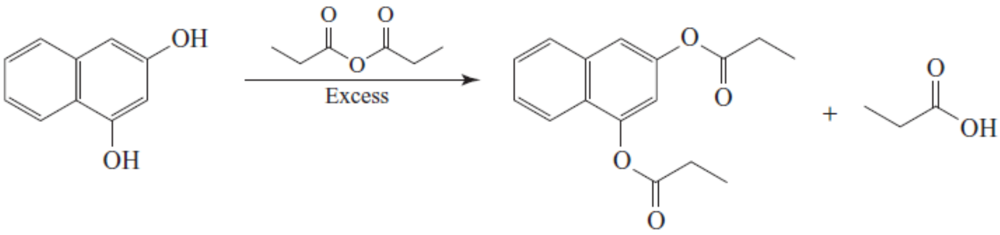

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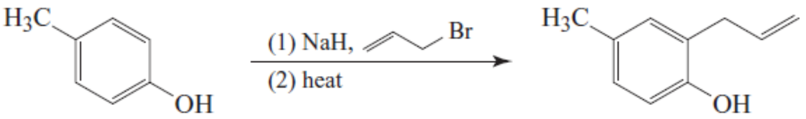

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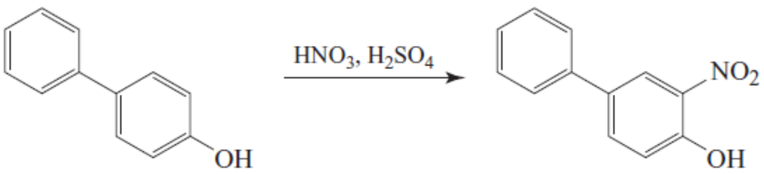

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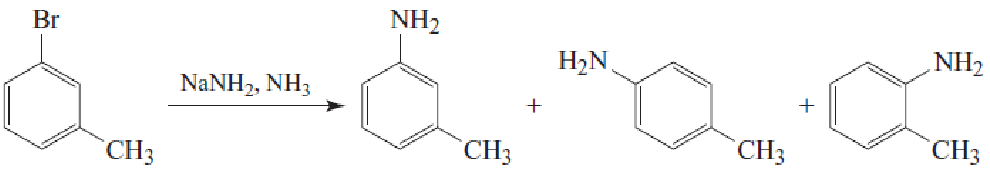
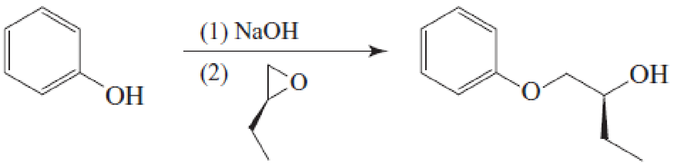
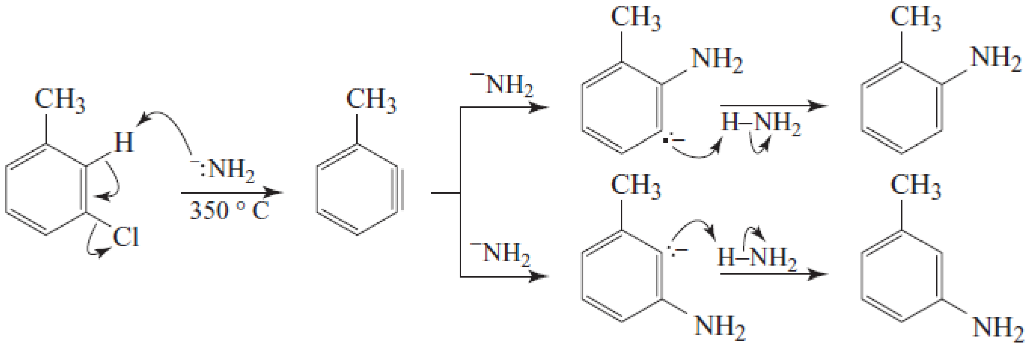
(h) 

(i) 

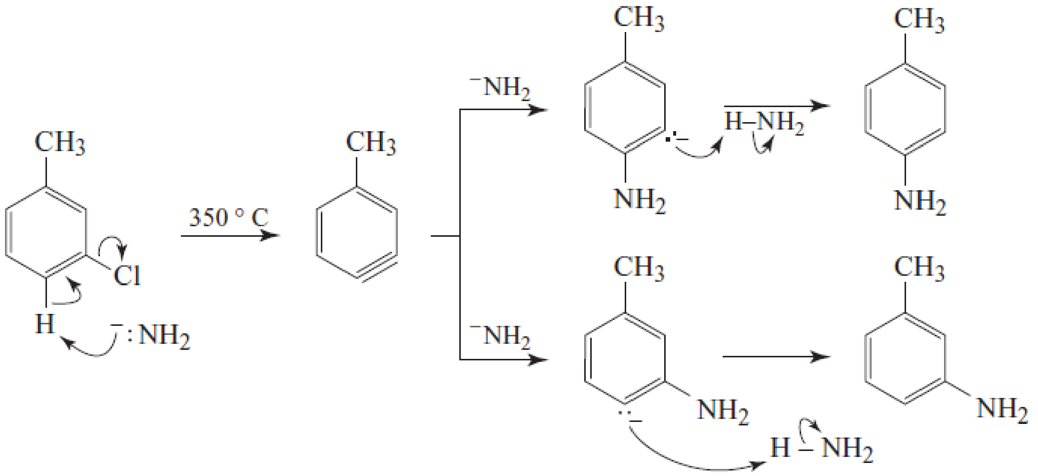
Mechanisms and Synthesis

19.14

Both *o*- and *m*-toluidine are formed in the following way:



Both *m*- and *p*-toluidine are formed from another benzyne-type intermediate.



19.15

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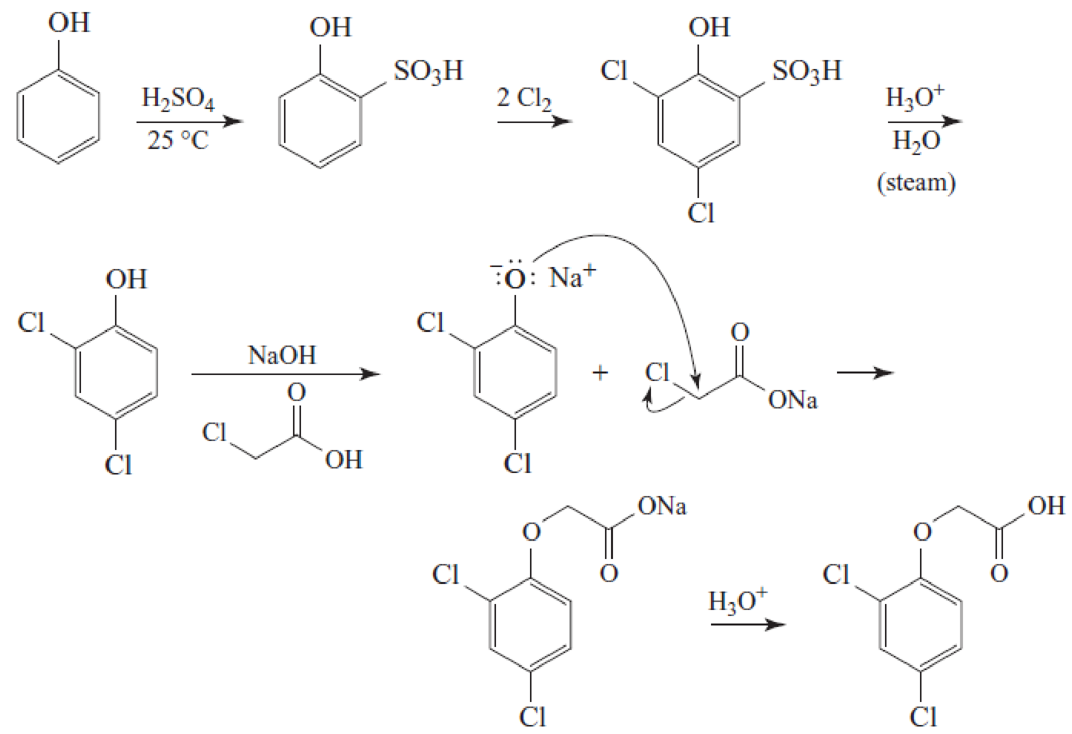
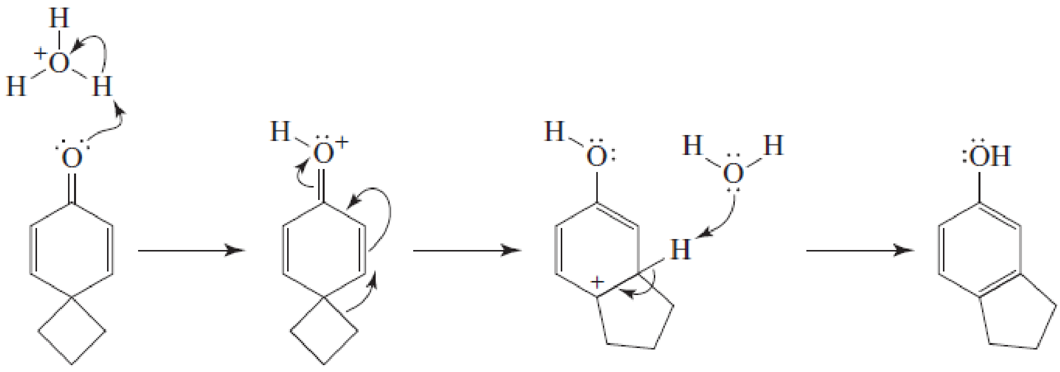


2,4-D

19.16



19.17

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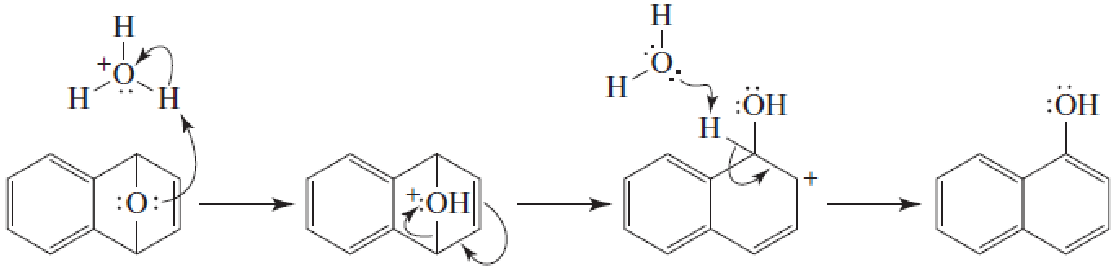
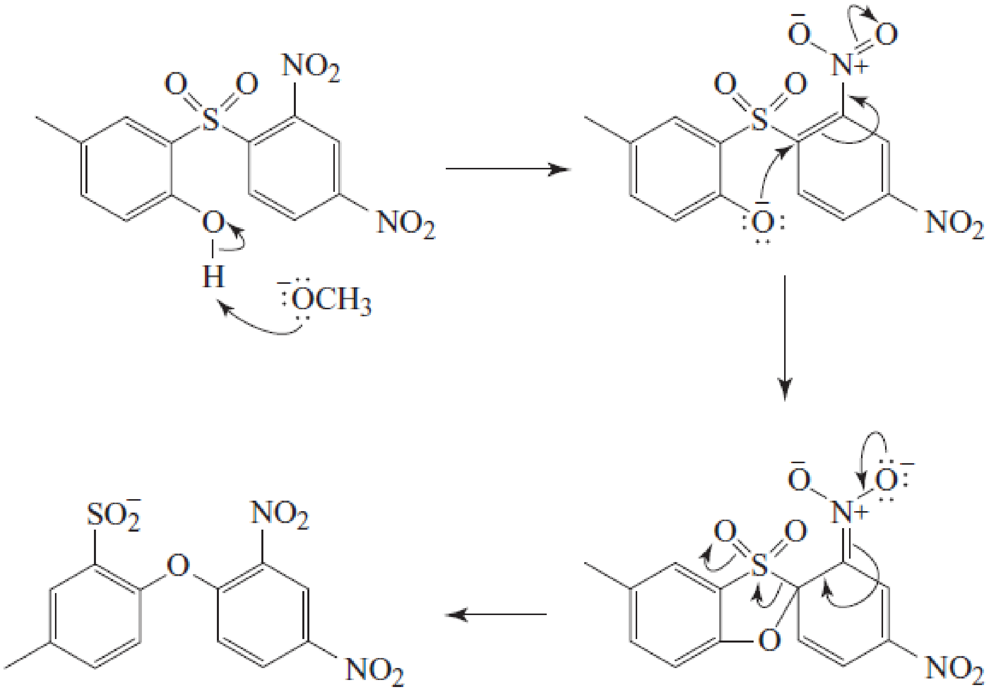
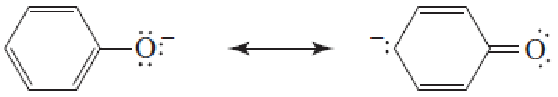


19.18



19.19

The phenoxide ion has nucleophilic character both at the oxygen and at the carbon para to it; it is ambident.



The benzyne produced by the elimination phase of the reaction can then undergo addition by attack by either nucleophilic center: reaction at oxygen producing **1** (diphenyl ether), and reaction at carbon producing **2** (4-hydroxybiphenyl).

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<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (b) It is Kolbe Schmitt reaction, CO_2 will undergo an electrophilic aromatic substitution at o position with respect to the stronger activating group OH.

2.**(c)** P is formed by Friedel Crafts alkylation, involving rearrangement of carbocation from n-propyl to iso-propyl carbocation. P undergoes the Cumene-Phenol process (or Hock process) for preparation of Phenol from Cumene (P) alongside formation of acetone.

3. (c) Same solution as 2.

4. **(b)** The benzene ring in phenol is highly activated toward electrophilic substitution and hence attempts to directly nitrate it result in charring and copious evolution of oxides of nitrogen. To reduce the reactivity, the phenol is first sulfonated and thus the nitration is comparatively smoother. Ipso substitution of -SO3 groups occurs.

5. **(a)** In basic medium, phenol converts to phenoxide which is a stronger activating group than amine and thus azo coupling takes place according to the directing influence of OH.

6. **(d)** Phenol decolorizes bromine water (EAS reaction) while ethanol does not. Ethanol gives iodoform test (forms yellow ppt.) while phenol does not. The ferric chloride forms a violet colored complex with the phenol.

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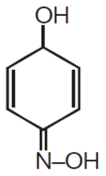
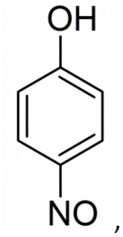
7. **(c)** The compound I is formed by Kolbe Schmitt reaction in which Carboxylic acid group is introduced at ortho position to OH. The compound II is formed by acylation of OH group.

8. **(a)** The SNAr will take place at para position with respect to the strong electron withdrawing nitro group.

9. **(b)** The addition of HBr to alkene will take place as per Markovnikov rule.

10. **(a)** Here, P is 

, Q is 

, while R is phenol.

11. **(c)** Electron withdrawing groups increase reactivity towards SNAr.

12. **(a)** Dow's process is used for the manufacture of phenol.

13. **(d)** Aryl halide reactivity (in SNAr): -F > -Cl > -Br > -I. The more electronegative the group, the greater is the ability to attract electrons which increases the rate of formation of the cyclohexadienyl anion.

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14. **(d)** Electron withdrawing group in the diazonium increase its reactivity towards azo-coupling.

15. **(c)** Electron withdrawing group at o/p position increase reactivity towards SNAr. F is more reactive than Br towards SNAr.
16. **(b)** In SNAr, electron donating group in the nucleophile and electron withdrawing group in the Aryl halide increases the rate of reaction.
17. **(b)** o-nitrophenol has intramolecular H bonding.
18. **(d)** Electron withdrawing group at o/p position increase reactivity towards SNAr.
19. **(d)** The bromine water is decolorized and Br is substituted in place of H at all the o and p positions.
20. **(a)** In P, nitro group is introduced by nitration, while in the second reaction, the SNAr will take place at o/p position with respect to the –M nitro group.
21. **(b)** Azo-coupling will occur at para position with respect to the electron donating OH group of phenol.

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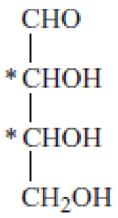
Chapter 20: Carbohydrates

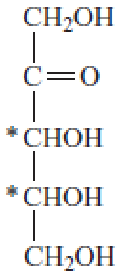
Practice Problems

20.1

(a) Two,

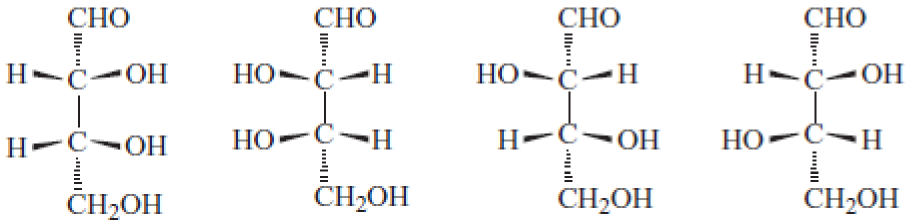


(b) Two,

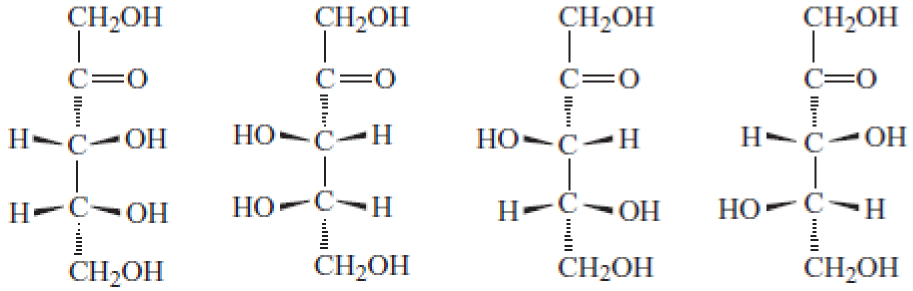


(c) There would be four stereoisomers (two sets of enantiomers) for each general structure: $2^2 = 4$.

20.2



D L D L



D L D L

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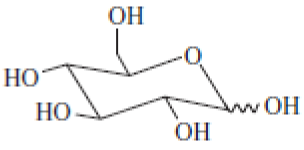
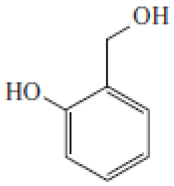
20.3

(a)



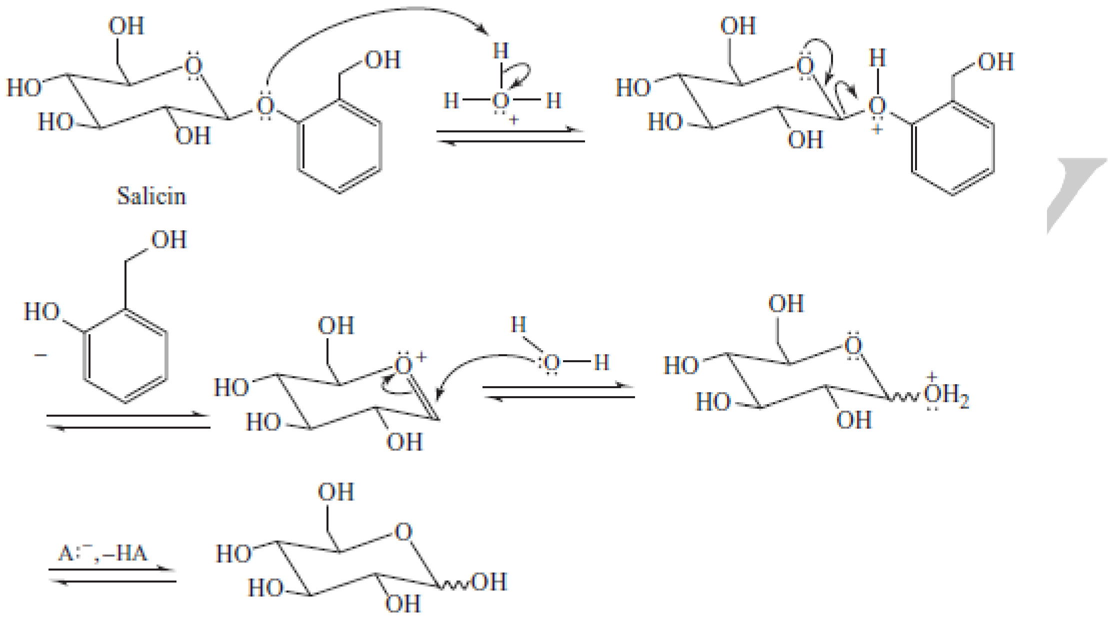
D-(+)-Glucose

and



2-Hydroxybenzyl alcohol

(b)



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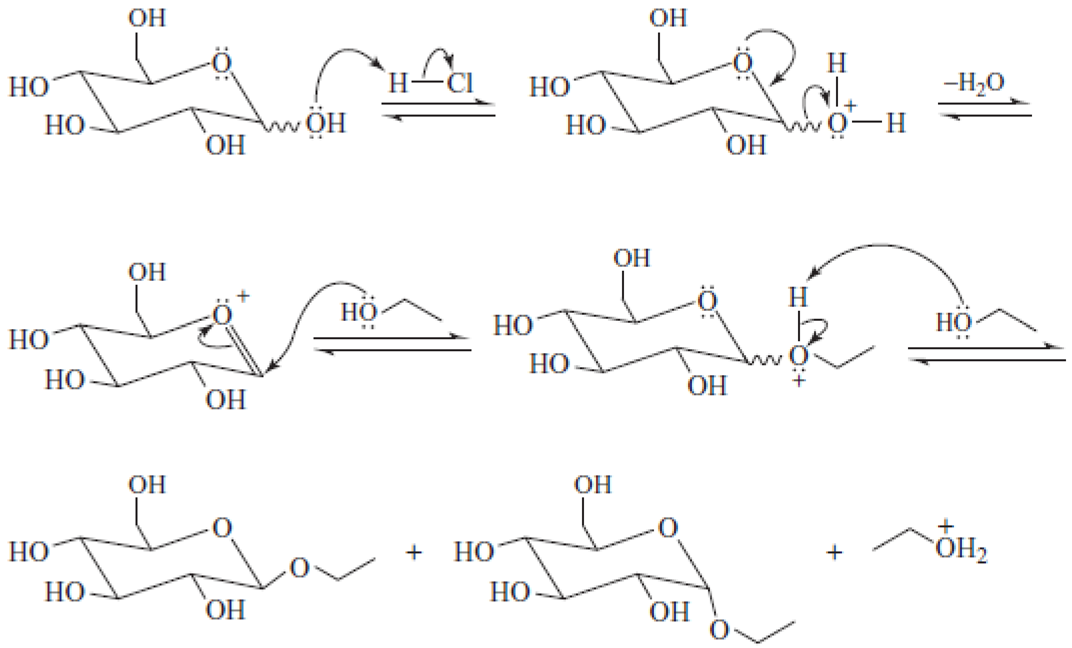
20.4

Dissolve D-glucose in ethanol and then bubble in gaseous HCl.



20.5

α-D-Glucopyranose will give a positive test with Benedict's or Tollens' solution because it is a cyclic hemiacetal. Methyl α-D-glucopyranoside, because it is a cyclic acetal, will not.

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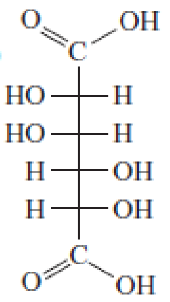
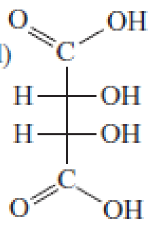
20.6

(a) Yes (b)

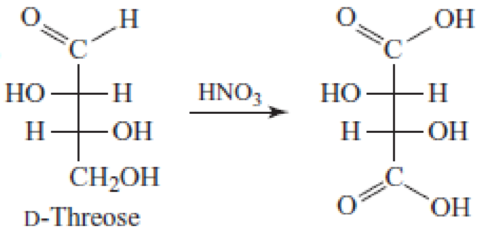


D-Mannaric acid

(c) Yes (d)



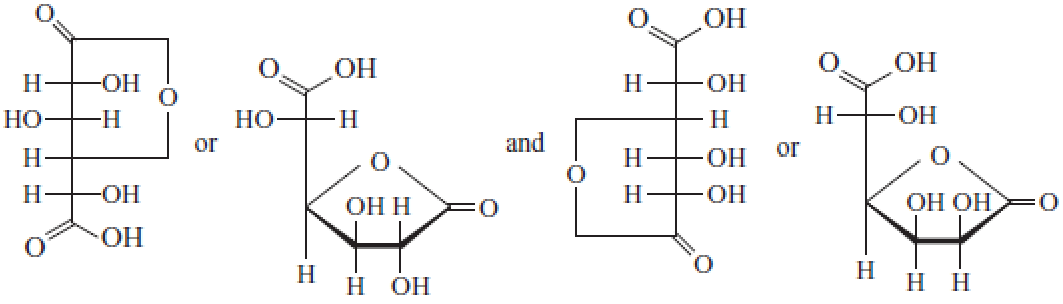
(e) No (f)



D-Threose D-Tartaric acid

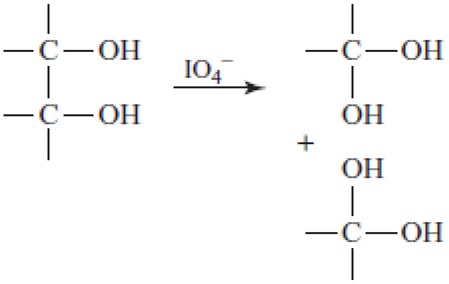
(g) The aldaric acid obtained from D-erythrose is *meso*-tartaric acid; the aldaric acid obtained from D-threose is D-tartaric acid.

20.7



20.8

One way of predicting the products from a periodate oxidation is to place an —OH group on each carbon atom at the point where C—C bond cleavage has occurred:



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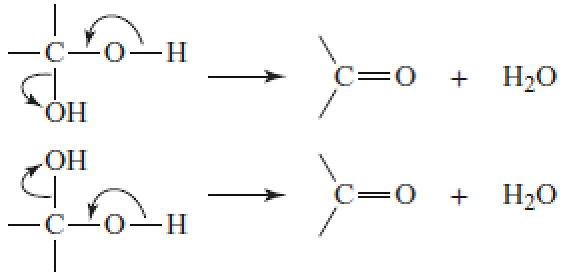
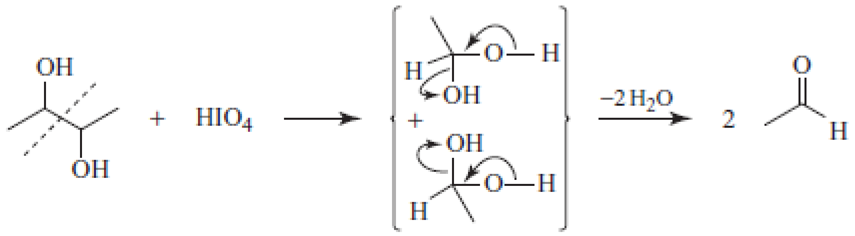
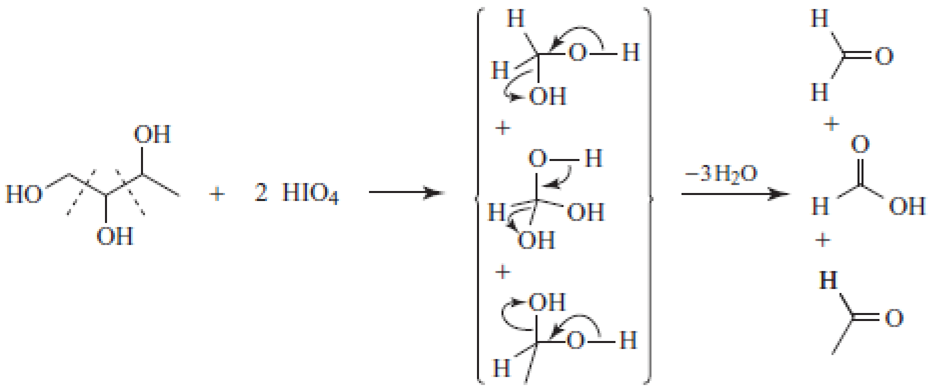
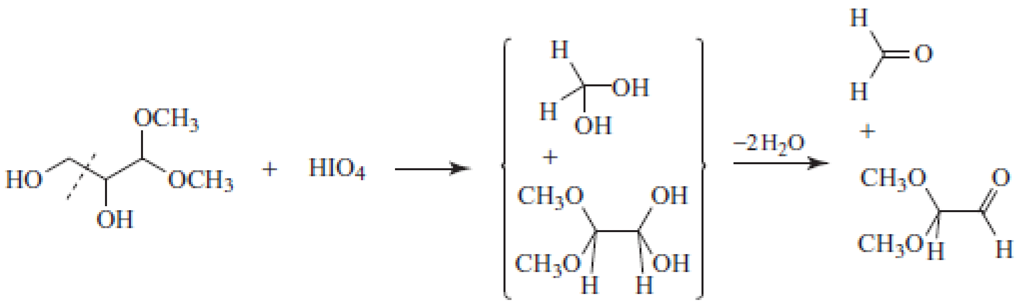
Then if we recall (Section 16.7A) that *gem*-diols are usually unstable and lose water to produce carbonyl compounds, we get the following results:



Let us apply this procedure to several examples here while we remember that for every C—C bond that is broken 1 mol of HIO_4 is consumed.

(a) 

(b) 

(c) 

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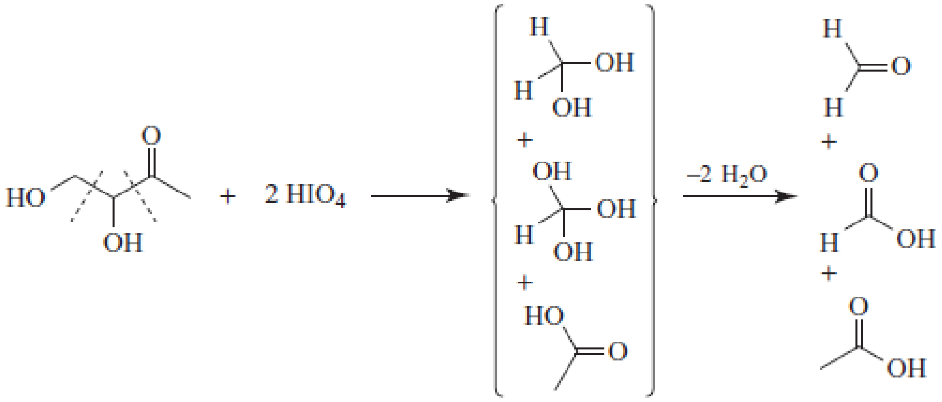
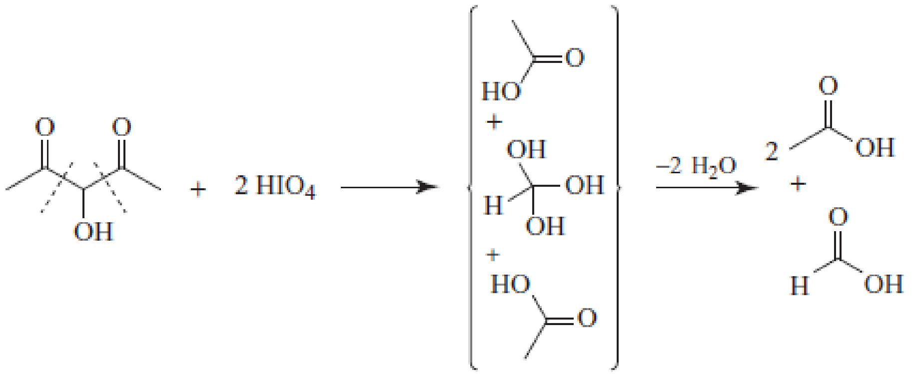
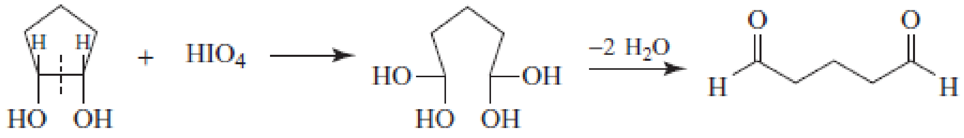
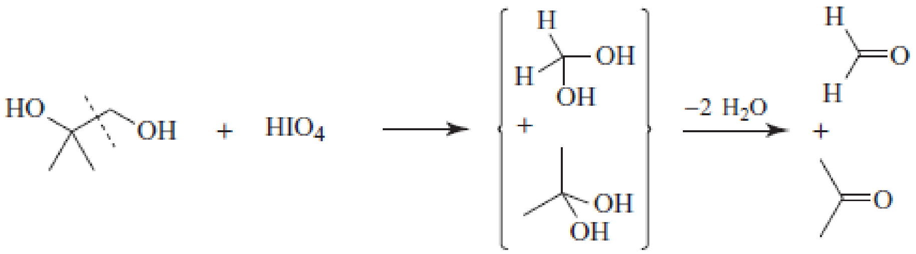
(d) 

(e) 

(f) 

(g) 

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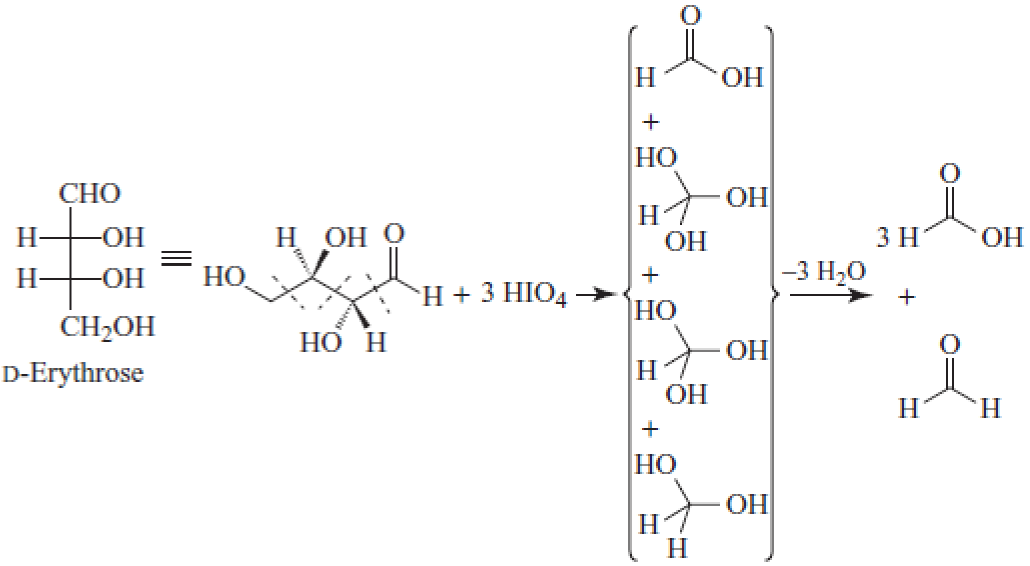
(h)



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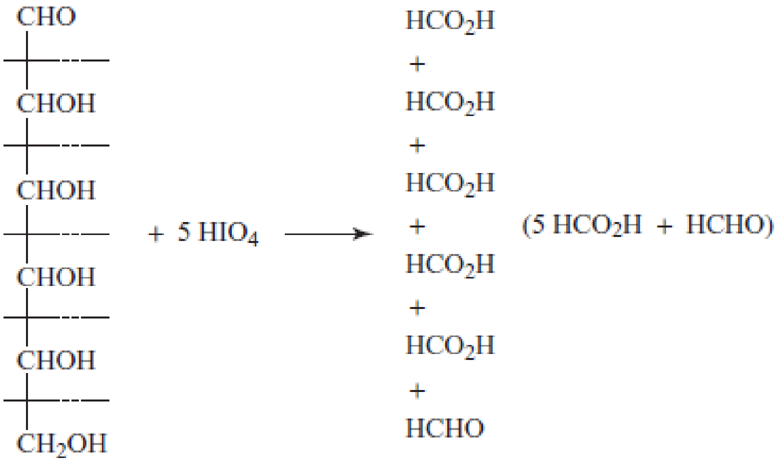
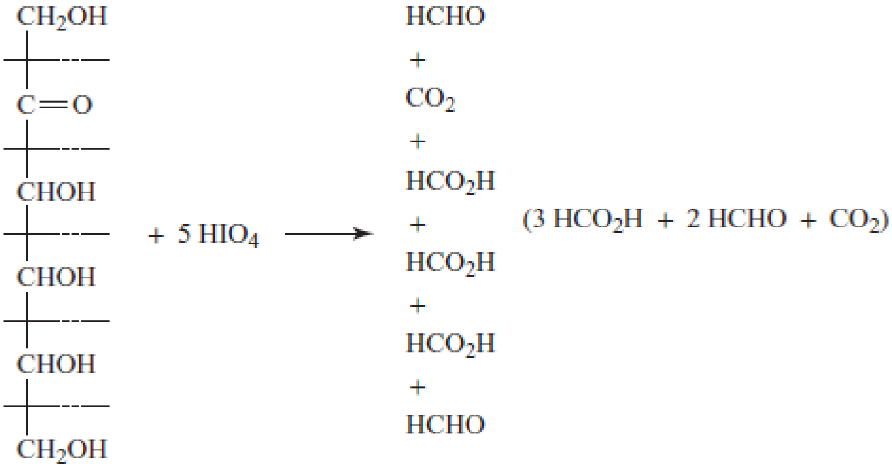
20.9

Oxidation of an aldohexose and a ketohexose would each require 5 mol of HIO_4 but would give different results.



Aldohexose



Ketohexose

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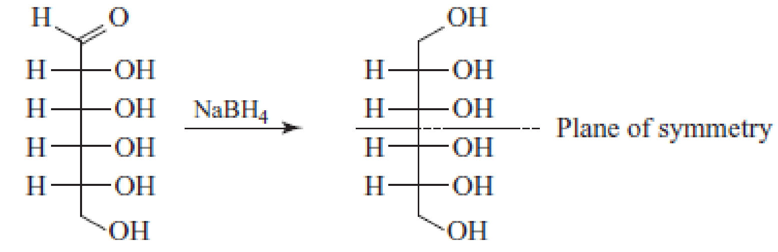
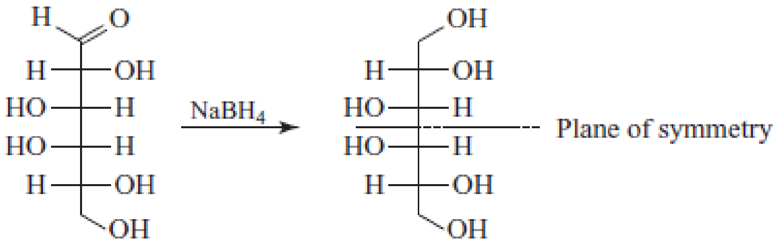
20.10

(a) Yes, D-glucitol would be optically active; only those alditols whose molecules possess a plane of symmetry would be optically inactive.

(b)



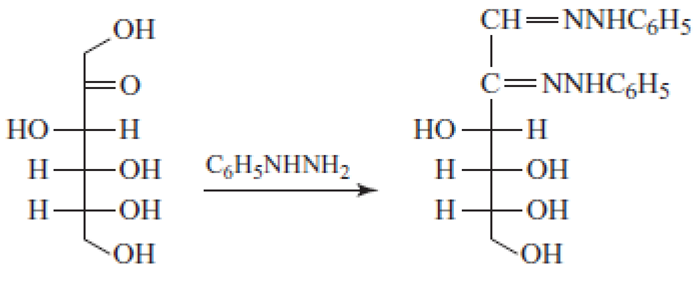
Optically inactive



Optically inactive

20.11

(a)



(b) This experiment shows that D-glucose and D-fructose have the same configurations at C3, C4, and C5.

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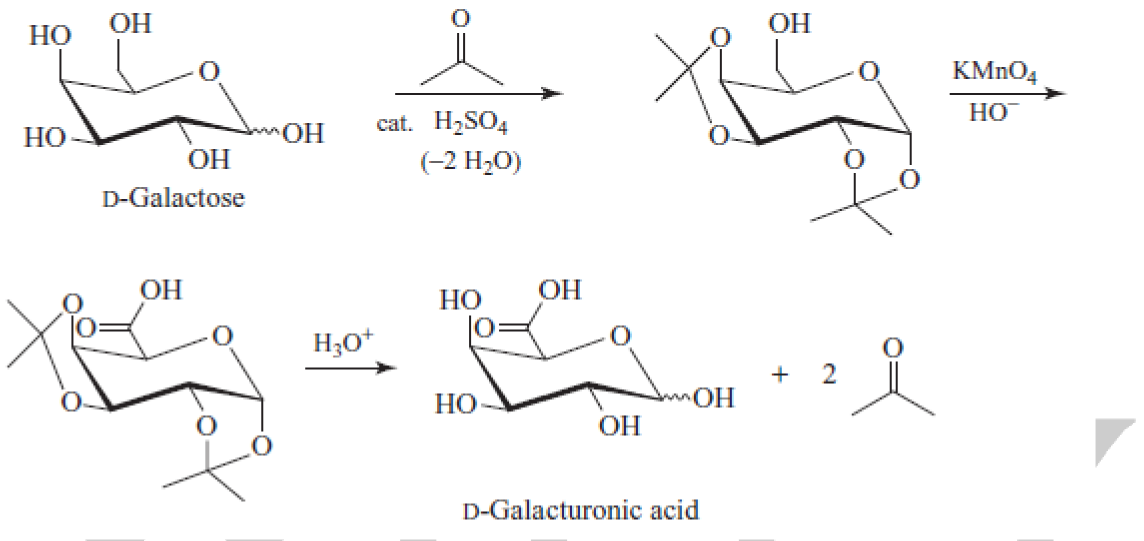
20.12



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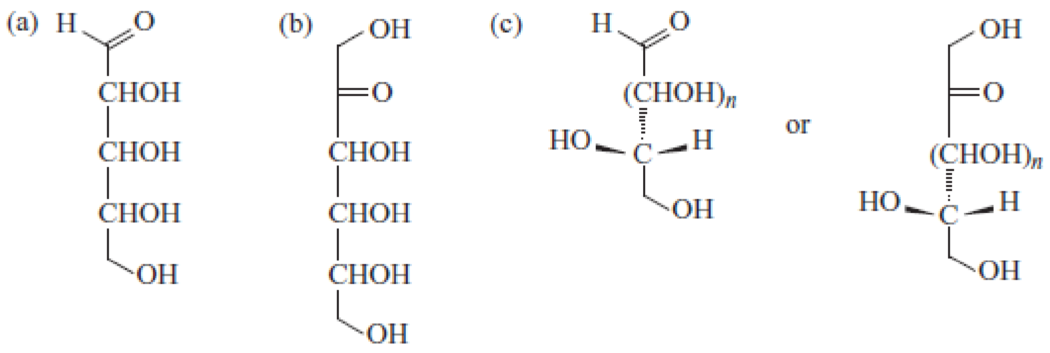
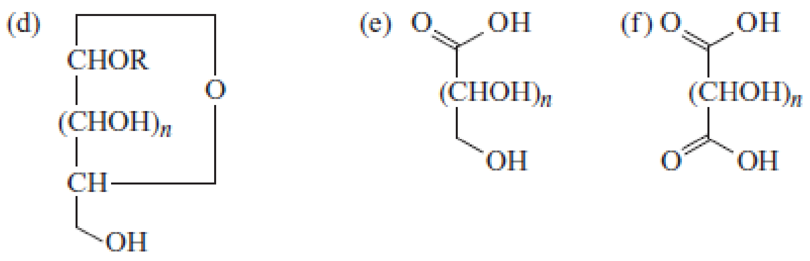
REVIEW PROBLEMS

20.13





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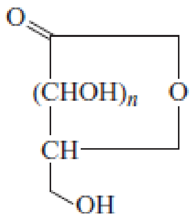
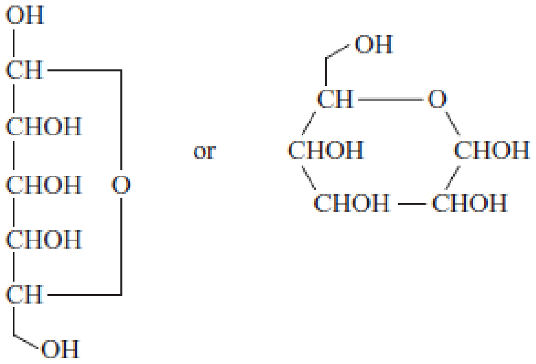
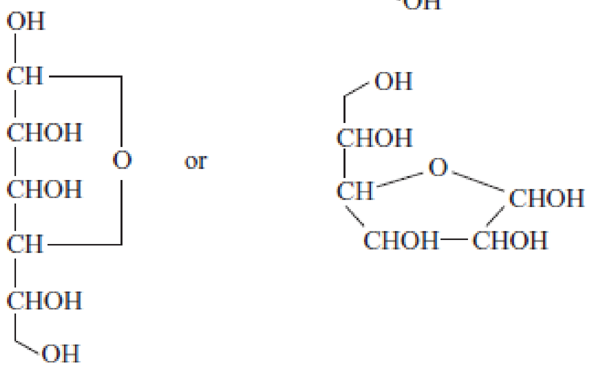
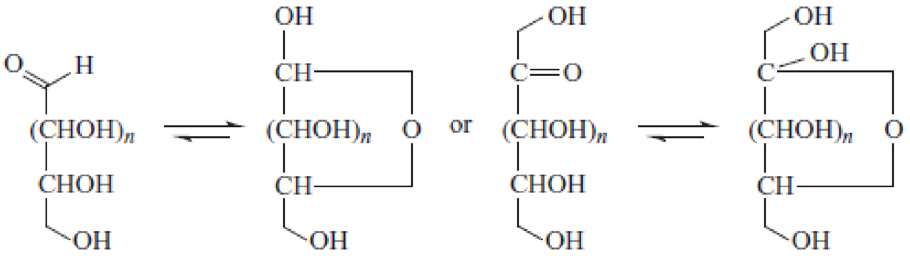
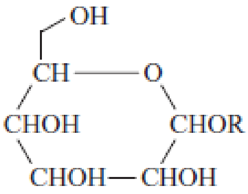
(g) 

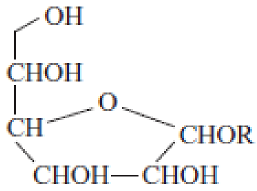
(h) 

(i) 

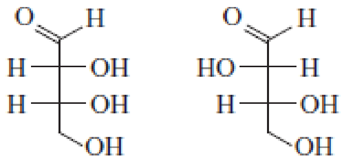
(j) Any sugar that has a free aldehyde or ketone group or one that exists as a cyclic hemiacetal. The following are examples:



(k) 

(l) 

(m) Any two diastereomers that differ in configuration at only one chirality center. (See Section 22.8.) D-Erythrose and D-threose are examples.



D-Erythrose D-Threose

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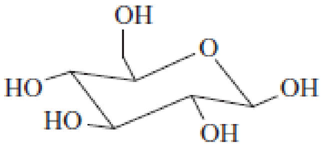
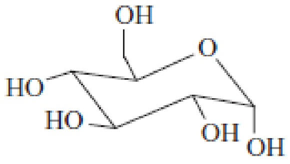
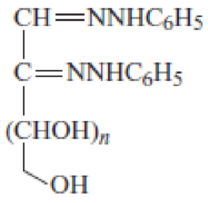
(n) Cyclic sugars that differ in configuration only at the hemiacetal or acetal carbon. The following are examples:



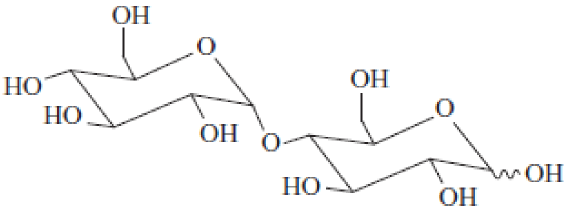
and



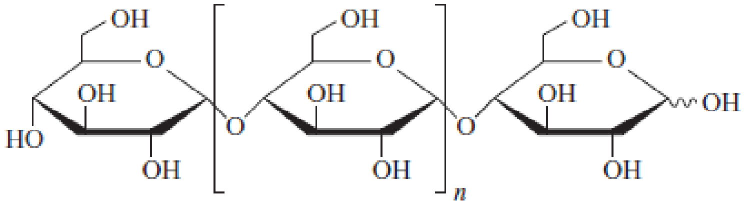
(o)



(p) Maltose is an example:



(q) Amylose is an example:



(r) Any sugar in which all potential carbonyl groups are present as acetals (i.e., as glycosides). Sucrose (Section 22.12A) is an example of a nonreducing disaccharide; the methyl D-glucopyranosides (Section 22.4) are examples of nonreducing monosaccharides.

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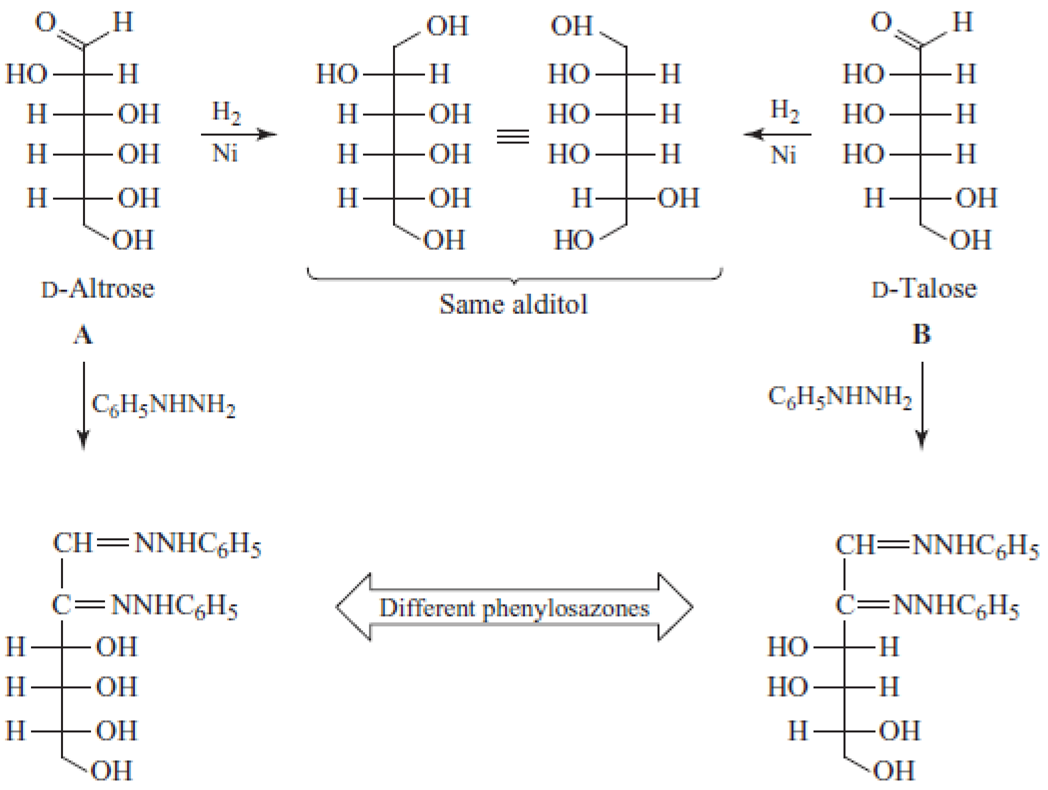
20.14

A is D-altrose, **B** is D-talose, **C** is D-galactose.



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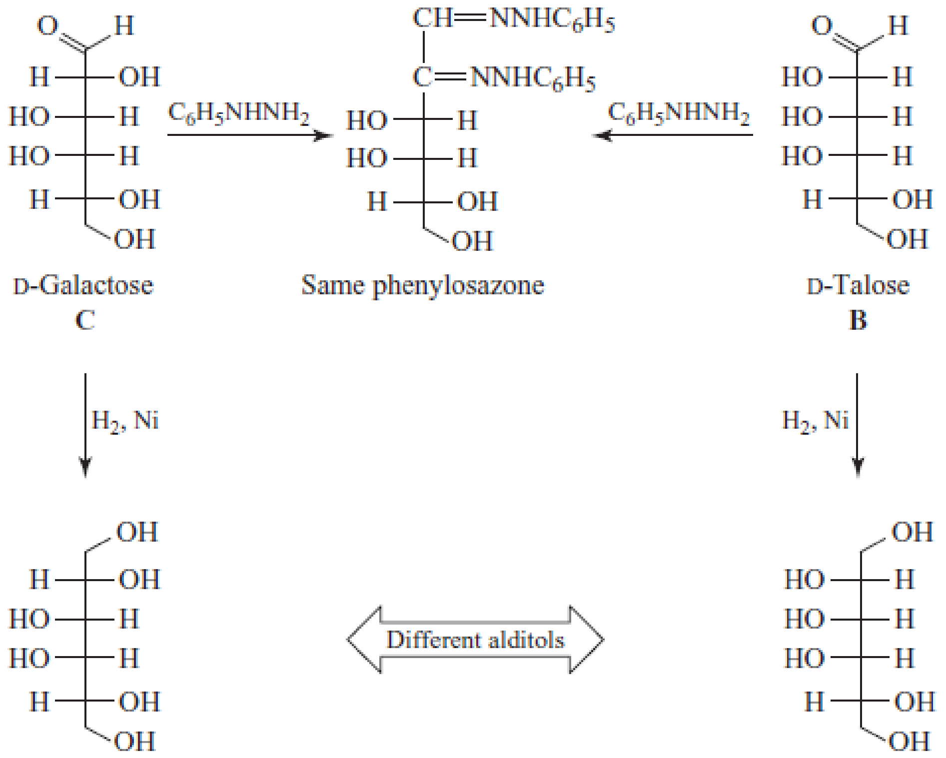
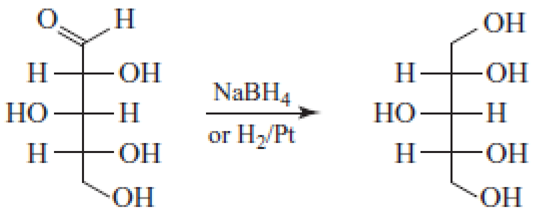


(*Note*: If we had designated D-talose as **A**, and D-altrose as **B**, then **C** is D-allose).

20.15



D-Xylose D-Xylitol

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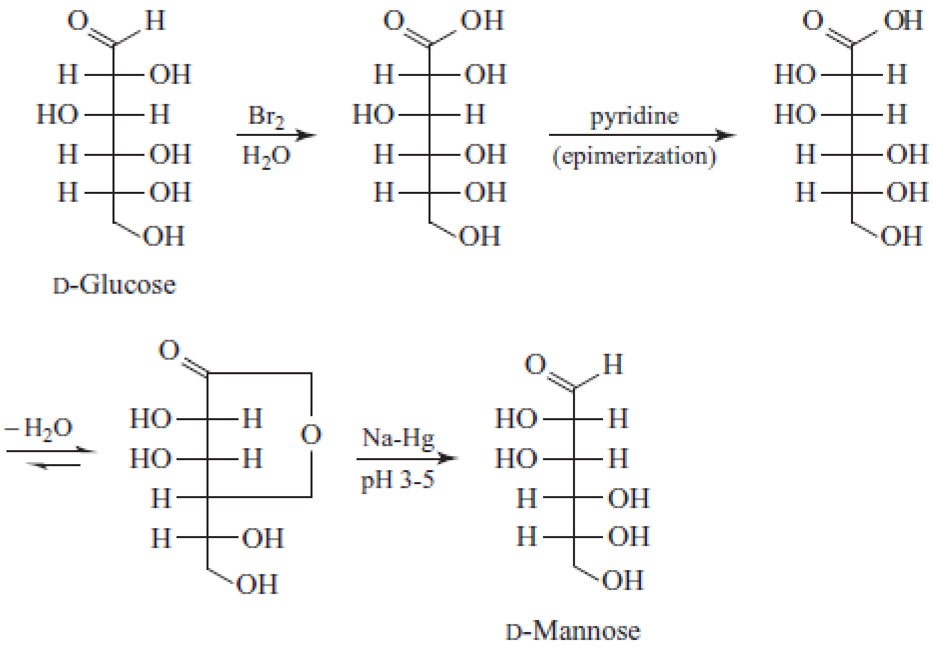
20.16



20.17

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(a) Tollens' reagent or Benedict's reagent will give a positive test with D-glucose but will give no reaction with D-glucitol.

(b) D-Glucaric acid will give an acidic aqueous solution that can be detected with blue litmus paper. D-Glucitol will give a neutral aqueous solution.

(c) D-Glucose will be oxidized by bromine water and the red brown color of bromine will disappear. D-Fructose will not be oxidized by bromine water since it does not contain an aldehyde group.

(d) Nitric acid oxidation will produce an *optically active* aldaric acid from D-glucose but an *optically inactive* aldaric acid will result from D-galactose.

(e) Maltose is a reducing sugar and will give a positive test with Tollens' or Benedict's solution. Sucrose is a nonreducing sugar and will not react.

(f) Maltose will give a positive Tollens' or Benedict's test; maltonic acid will not.

(g) 2,3,4,6-Tetra-*O*-methyl-β-D-glucopyranose will give a positive test with Tollens' or Benedict's solution; methyl β-D-glucopyranoside will not.

(h) Periodic acid will react with methyl α-D-ribofuranoside because it has hydroxyl groups on adjacent carbons. Methyl 2-deoxy-α-D-ribofuranoside will not react.

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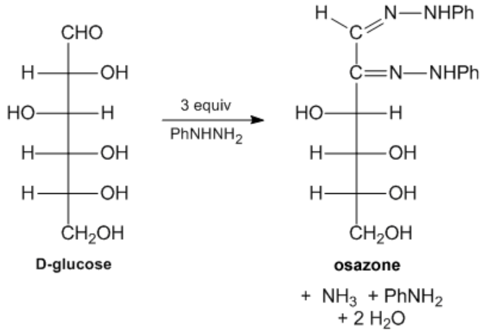
<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1.(a) Glucose is the monomer unit of Cellulose.

2.(a) Three moles are used. Glucose with phenylhydrazine gives glucosephenylhydrazone by elimination of a water molecule. Then one equivalent of glucosephenylhydrazone reacts with two equivalents of phenylhydrazine (excess), one is involved in oxidizing the alpha carbon to a carbonyl group, and the second phenylhydrazine involves removal of one water molecule with the formyl group of that oxidized carbon.



3.(b) All monosaccharides are reducing sugar.

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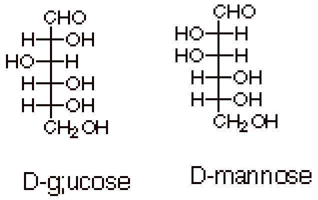
4.(d) To form acetal linkage, use methanol in HCl.

5.(d) Acetal linkage is formed.

6.(c) It is present in pyranose form.

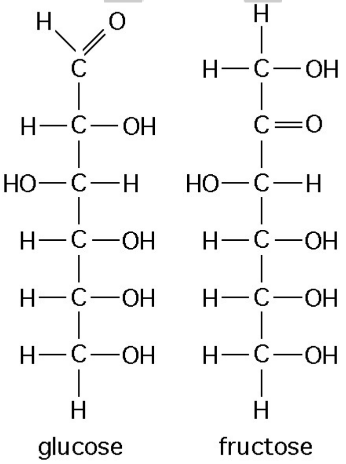
7.(d) Both are reducing monosaccharides.

8.(c) Epimers differ in configuration about one carbon atom.



9.(a) All OH groups of cellulose (polymer of Glucose) will undergo acetylation.

10.(c) Anomers are diastereoisomers of cyclic forms of sugars differing in the configuration at the anomeric carbon (C-1 atom of an aldose or the C-2 atom of a 2-ketose).



11.(b) Aldehyde, α-hydroxy ketone and hemiacetal give positive Tollen's test.

12.(c) Maximum OH groups are at equatorial position.

13.(c) Sucrose is disaccharide.

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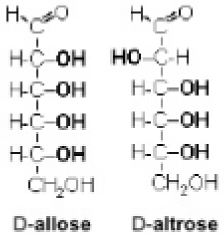
14.(c) Formation of ozone involves only C1 and C2 carbon atoms. The rest of the carbon atoms remain unaffected.



15.(d) Hydrolysis gives D-glucose and D-fructose.

<H2> Multiple Correct Choice Type

1.(a),(c),(d) On the basis of stereochemistry at the last asymmetrical carbon.

2.(b),(c) Hemiacetal in Y and α and β linkages respectively in X and Y.

<H2> Linked Comprehension Type

1.(b) Anomers are stereoisomer at hemiacetal or acetal C.

2.(a) On the basis of stereochemistry at the last asymmetrical C.

3.(d) All are tautomers to each other.

<H2> Integer Type

1.(5) D-Mannose, D-Fructose, D-Gulose, D-ldose, D-Galactose.

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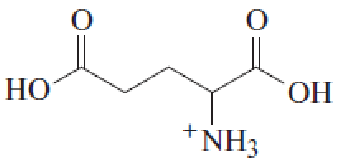
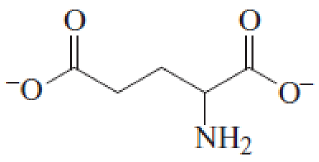
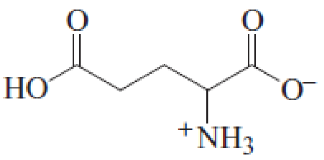
Chapter 21: Amino acids and Proteins

Practice Problems

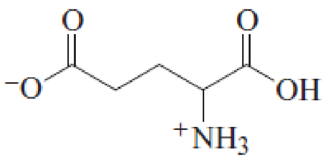
21.1

(a) 

(b) 

(c) 

predominates at the isoelectric point rather than



because of the acid-strengthening inductive effect of the α-aminium group.

(d) Since glutamic acid is a dicarboxylic acid, acid must be added (i.e., the pH must be made lower) to suppress the ionization of the second carboxyl group and thus achieve the isoelectric point. Glutamine, with only one carboxyl group, is similar to glycine or phenylalanine and has its isoelectric point at a higher pH.

21.2

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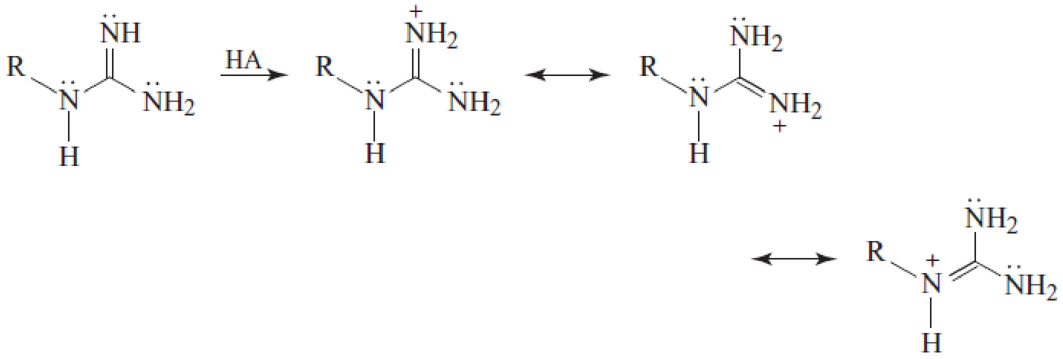
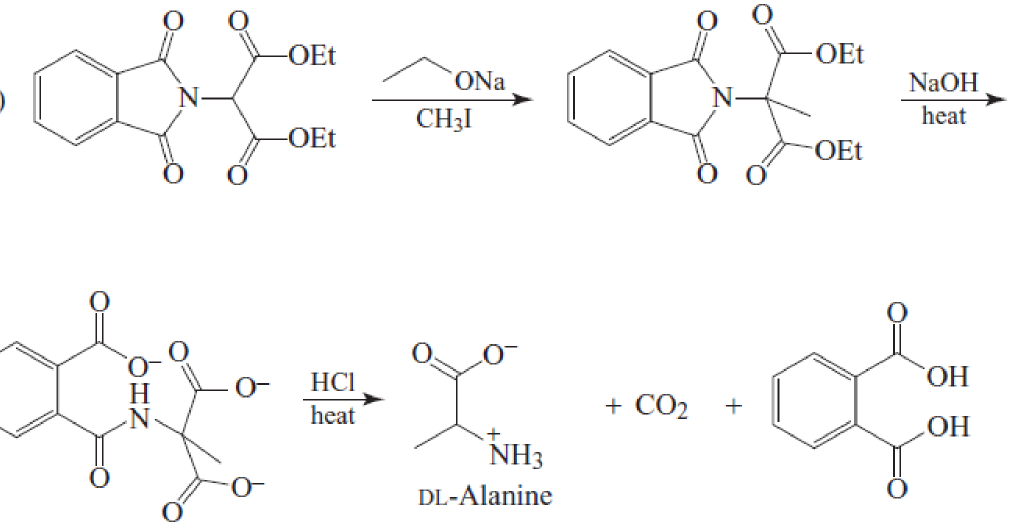
The conjugate acid is highly stabilized by resonance.



21.3

(b)



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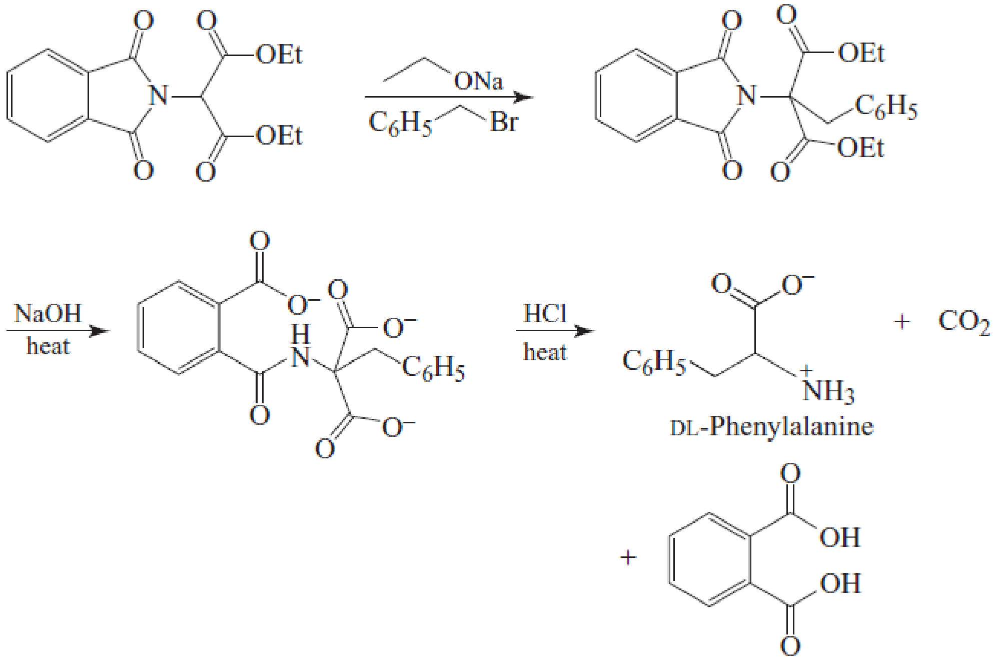

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21.4

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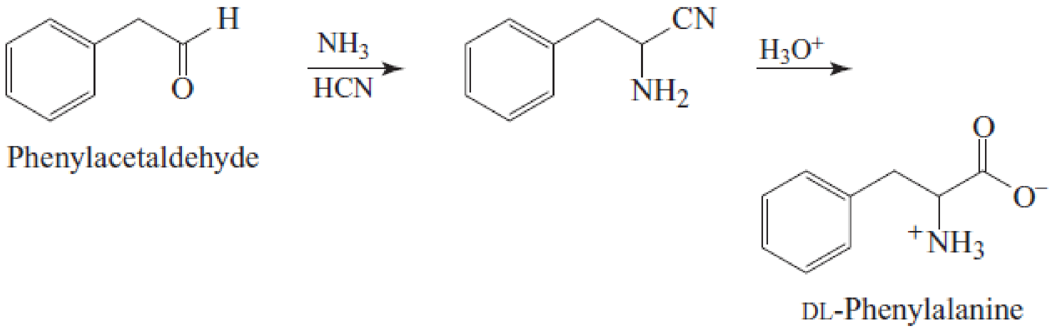
(a)



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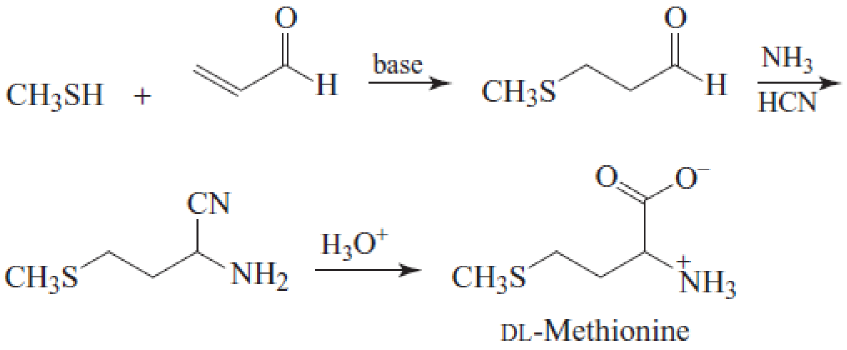

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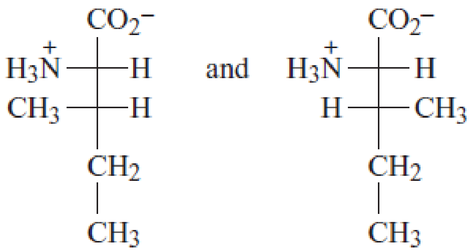
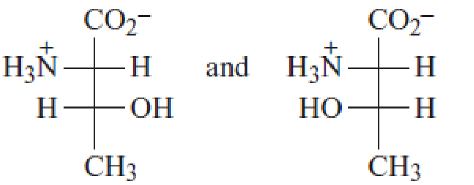
REVIEW PROBLEMS

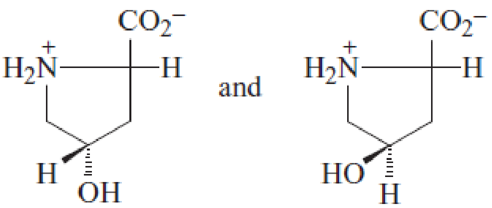
21.5

(a) Isoleucine, threonine, hydroxyproline, and cystine.

(b)







(With cystine, both chirality centers are α-carbon atoms; thus, according to the problem, both must have the L-configuration, and no isomers of this type can be written.)

(c) Diastereomers

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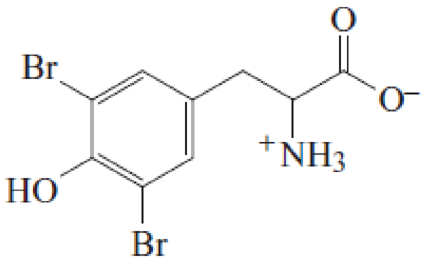
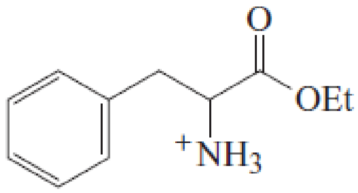
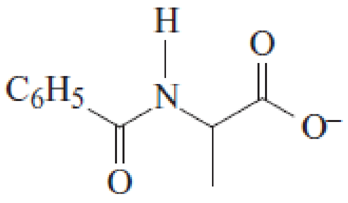
21.6

(a) 

(b) 

(c) 

21.7

At pH 2–3 the γ-carboxyl groups of polyglutamic acid are uncharged. (They are present as $-CO_2H$ groups.) At pH 5 the γ-carboxyl groups ionize and become negatively charged. (They become γ-CO_2^- groups.) The repulsive forces between these negatively charged groups cause an unwinding of the α helix and the formation of the random coil.

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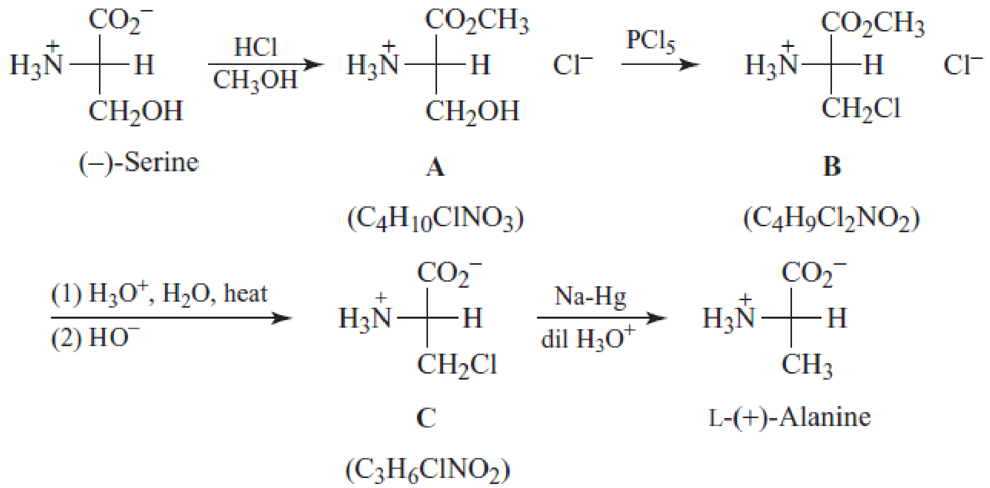
21.8

(a)



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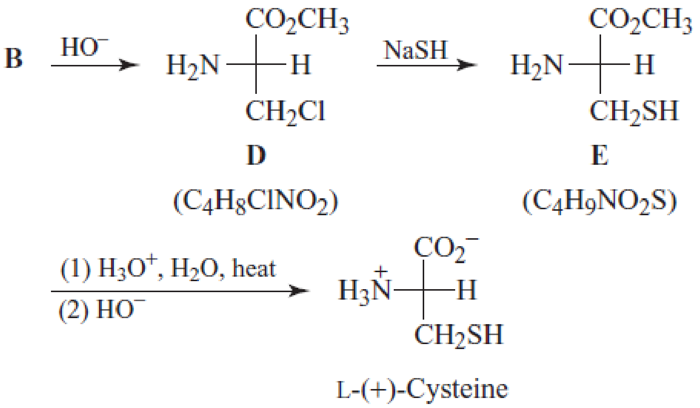

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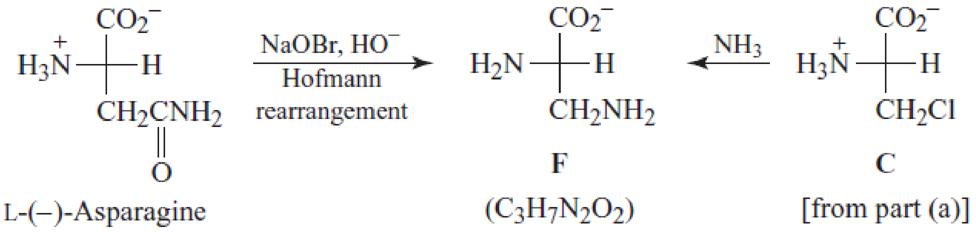

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<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. **(d)** Condensation is between the carboxylic group and the amine group to form amide.

2. (c) The compound must be cyclic so that all N are present in secondary form (diazonium is prepared by primary N).

3. (b) Each of the 100 amino acid of the protein can be chosen from 20 choices.

4. **(d)** Keto-enol is not possible in d.

5. (a) Proteins is peptide linkage of α amino acid.

6. **(d)** For any amino acid, if pI = 7, then both will be in ionic form.

7. (c) Proton will attack most basic site.

8. **(b)** Proteins is peptide linkage of α amino acid.

9. (b) In nature, most amino acids are present in L configuration.

10. (c) At isoelectronic point, net charge is 0.

11. (d) Peptide linkage is amide linkage.

12. (d)

13. (a) In Fischer representation, at horizontal position NH_2 must be on the left side and acid at top of vertical position.

14.(c) For amino acids with acidic side chains by taking the average of p*K*a1 and p*K*a3.

15. (b) The pH<pI.

16.(a) In electric field, isoelectric point.

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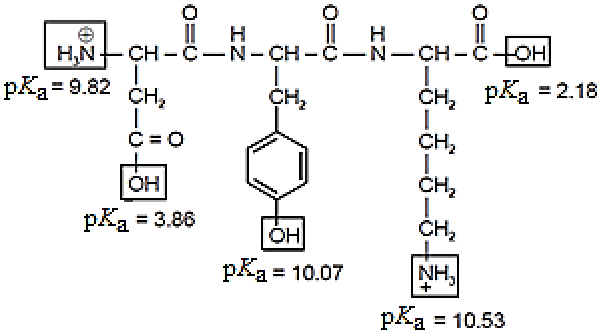
<H2> Integer Type

1.
(0) Both the carboxylic groups will lose a proton. Thus, net charge will be zero.



2.
(2) It is acidic amino acid having two carboxylic groups.

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<H2> **Matrix Match Type**

1.
a→(p, r); b→(q, s); c→(q, s); d→(p, r)

Apply CIP rules to determine R/S and stereochemistry of natural product to determine D/L.

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Chapter 22: Carbene and Carbenoids

<H1> Additional Objective Questions

<H2> Single Correct Choice Type

1. **(b)** Riemer Tiemann takes place in basic medium.

2. **(a)** The Carbylamine reaction (Hoffman's isocyanide test) involves formation of carbine intermediate.

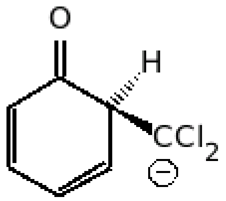
3. **(b)** The unpleasant smell is due to formation of isocyanide, only primary amine will give the test (Hofmann's isocyanide test).

4. **(b)** Formyl group (CHO MM=29) is added and one H (MM=1) is removed.

5. **(c)** Isocyanide is formed which has offensive odour.

6. **(c)** Instead of CHO, we get COOH group at the ortho position of OH.

7. **(a) Correction!!** The intermediate is shown below, instead of 3 Cl, we have carbanion with 2 Cl.

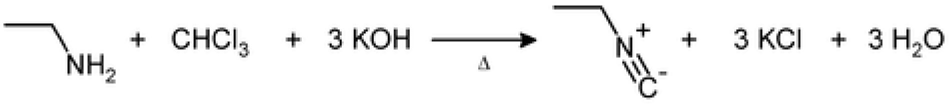


8. **(b)** Primary amine will give positive isocyanide test.

9. **(a)** It is Riemer Tiemann reaction.

10. **(a)** It is secondary amine, and only primary amines give the test.

11. **(c)**



12. **(b)** First is Riemer Tiemann reaction while the second is Isocyanide test.

13. **(c)** Carbon tetrachloride introduces carboxylic group at ortho position to OH.

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14. **(c)**The CHO group is introduced at o position to OH in Riemer Tiemann reaction.

15. **(a)** It is Hofmann's isocyanide test.

16. **(a)** Dichloro carbene is formed as an intermediate.

<H2> Linked Comprehension Type

1. **(b)** It will undergo Riemer Tiemann due to electron donating activating groups attached to it.

2. **(c)** Dichloro carbene is the electrophile.

3. **(c)** The common ortho position of both the OH groups is the most activated amongst the four.

4. (c) Sodium hydroxide and chloroform ($CHCl_3$) are used for Riemer Tiemann reaction.

5. **(c)** Dichlorocarbene is the electrophile.

6. **(b)** Dichloro carbene attacks at ortho position followed by intramolecular proton transfer.

<H2> Matrix Match Type

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$a \rightarrow (q, s); b \rightarrow (q, s); c \rightarrow (q, s); d \rightarrow (p)$

1.

(a) Carbanion and carbene are intermediates in Riemer Tiemann reaction.

(b) Carbanion is formed in the first step upon removal of Br^+ from the molecule, and then carbene is formed by removal of Br^-.

(c) Carbene formation. First $^-CCl_3$ and CO_2 are released and then Cl^- gets removed from CCl_3 and dichloro carbene is formed.

(d) Carbocation is formed in the dehydration reaction (E1 mechanism).

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Chapter 23: Reactions of Nitrenes and Electron Deficient Oxygen

Practice Problems

1. (d) It is Hofmann Bromamide reaction, upto one mole of KOH, only one proton of amide will be substitute by Br.

2. (b) It is Beckmann Rearrangement reaction, group anti to the OH group will migrate.

3. (d) Only primary amide undergo Hofmann Bromamide reaction.

4. (a) **Correction!!** Replace a,b,c,d with 1,2,3,4. In first reaction, first step is isocyanide test while the second step is reduction. In second reaction, first step is Riemer Tiemann reaction while the second step is reduction.

5. (b) It is Hoffman Bromamide reaction and the amine will add to the same side as amide.

6. (c) First, Hofmann Bromamide reaction will take place followed by substitution of Cl by amine through SNAE (Substitution nucleophilic addition via elimination).

7. (a) It is Beckmann Rearrangement reaction, PCl_5 will act as Lewis acid.

8. (b) It is Beckmann Rearrangement reaction, group anti to the OH group will migrate.

9. (a) Hoffman Bromamide reaction followed by acetylation of amine.

10. (d) It is Carbylamine test (Hofmann Isocyanide test).

11. (a) It is Beckmann Rearrangement reaction, group anti to the OH group will migrate.

12. (b) X is oxime formed by elimination of water molecule, Y is formed by Beckmann Rearrangement in which amide is formed which then undergoes hydrolysis to form Carboxylic acid.

13. (b) It is Wolff rearrangement reaction.

14. (c) A is methyl amine formed by Hoffman Bromamide reaction while B is ethyl amine formed by reduction.

15. (a) A is Salicylic acid formed by Kolbe Schmitt reaction which undergoes acetylation of OH group to form 2-acetoxybenzoic acid or Aspirin.

16. (b) It is Wolff rearrangement reaction.

17. (b) It is Hofmann Broamide reaction.

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18. (c) It is oxidation reaction, amine is oxidised to nitro.

19. (c) Methyl group will migrate in the Beckmann rearrangement reaction to form A (N-methyl propanamide), which is then reduced by LAH from amide to amine.

20. (d) Isocyanide is also called carbylamine.

<H2> Linked Comprehension Type

1. (d) Br_2 and KOH are required, the base will abstract proton from the amide, and the anion will then attack bromine as nucleophile.

2. (d) Migration is the RDS in this reaction.

3. (b) Migration in Hofmann Bromamide is intramolecular only.

<H2> Matrix Match Type

a→(p, r,s) ; b→(q, r);c→(p, r, s); d→(p, r,s)

(a)- Hofmann Bromamide reaction, product A is Aniline. Since it is primary amine, hence it will give isocyanide test.

(b)- Reduction reaction. Since it is primary amine, hence it will give isocyanide test.

(c)- Beckmann reaction, group anti to OH will migrate. Since primary amine is product, hence it wil give isocyanide test.

(d)- Hofmann Bromamide reaction, product A is Aniline. Since it is primary amine, hence it will give isocyanide test.

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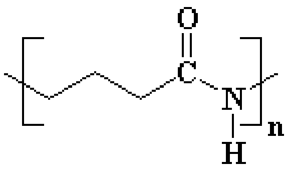
Chapter 24: Polymers

<H1> ADDITIONAL OBJECTIVE QUESTIONS

<H2> Single Correct Choice Type

1. (2) Polymers form by condensation of monomers.

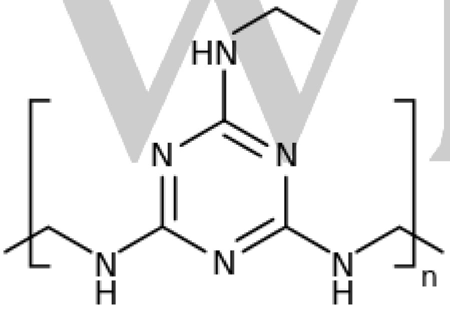
2.(3) Nylon is polymer of amide.

a. 

3. (2) H bonding is between the O and H.

4. (1) Plexiglass is homopolymer of methyl 2-methylpropenoate.

5. (3) Melamine structure is given below.



6. (1) Bakelite. A step-growth polymerization is a stepwise reaction between bi-functional or multi-functional monomers in which a high-molecular-weight polymer is formed.

7. (4) Chloroprene is the monomer unit.

8. (4) All polymers are macromolecules but all macromolecules are not polymers. Chlorophyll is macromolecule.

9. (1) Bakelite structure is given below.

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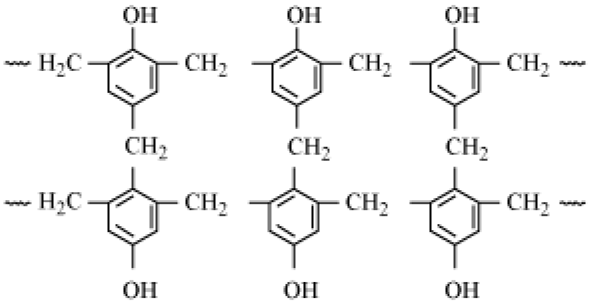


Bakelite

10. (3) Nylon-6 is polymer of caprolactum monomer unit.

11. (3) It is involved in free radical polymerisation.
12. (3) Wool is a polyamide.

13. (2) It is condensation polymer of melamine and formaldehyde.

14. (1) Formaldehyde acts as electrophile, so EAS reaction.

15. (2) Formaldehyde is not used in Nylon-6 because nylon-6 is polymer of caprolactum.

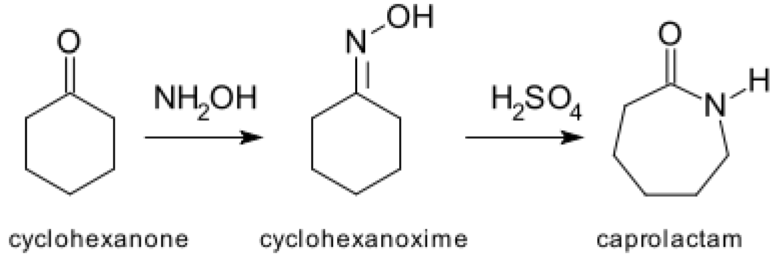
16. (1) Condensation polymer because condensation reaction is carried out.

17. (4) Polyacrylonitrile (PAN), also known as Creslan or Orlon.

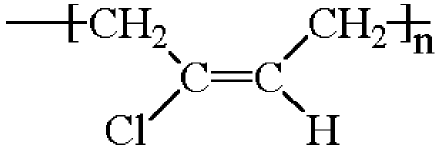
18. (1) Buna-S is addition polymer of styrene and butadiene.

19. (1) Bakelite is condensation polymer.

20. (1)



21. (2)



22. (2) Buna-S is addition copolymer of styrene and butadiene.

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23. (1) Glyptal is used in paints.

24. (4) Nylons are polyamides.

25. (4) The polymers (1),(2) and (3) are natural rubbers.

26. (3) Peptides are amide linkages, present in proteins.

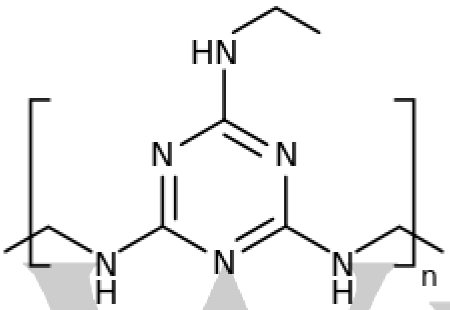
27. (1) Rubber is polymer of isoprene (2-methyl butadiene)

28. (4) RNA is polymer of nucleotide unit.

29. (2) Fibres have strong intermolecular forces (H bonding is present).

30. (4) Teflon is used.

31. (2) Melamine structure is given below.



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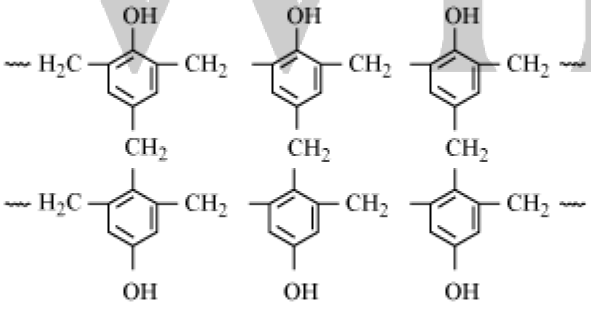
32. (1) Bakelite structure is given below.



Bakelite

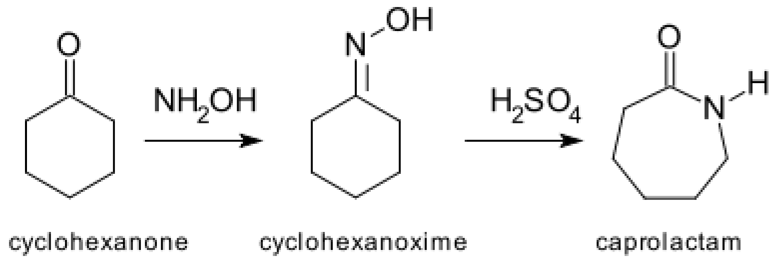
33. (1) Buna-S consists of 75% butadiene + 14% styrene.

34. (3) More than one monomer unit are present in both copolymer and heteropolymer.

35. (2)

A. Caprolactam	b. Nylon
B. Chloroprene	d. Synthetic rubber
C. Dimethyl terephthalate	a. Polyester
D. Methyl methacrylate	c. Perspex

36. (2)



37. (1) Macromolecule particles can be formed by condensation reaction.

38. (2)

39. (2) Acrilan is PAN.

40. (1) Vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by the addition of S.

41. (3) A. Coordination polymerization — c. Ziegler-Natta Catalyst

B. Free radical polymerization — d. Azo bis-isobutyronitrile

C. Addition polymerization — b. Nylon-6,6

D. Natural rubber — e. cis-1, 4-polyisoprene

42. (2) PDI = M_w/M_n, where M_w is the weight average molecular weight and M_n is the number average molecular weight.

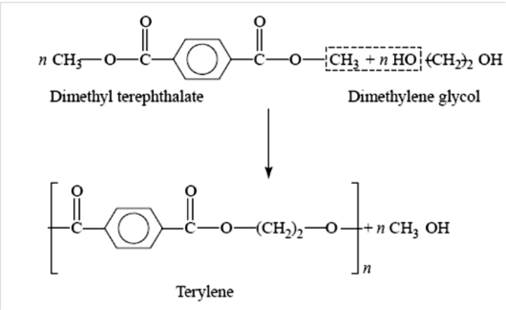
43. (4)

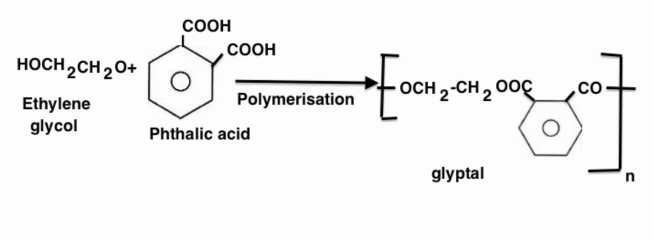
44. (3) Terylene or Dacron is polyester.

45. (3) The are made of polystyrene.

<H2> Multiple Correct Choice Type

1. (3),(4) Glyptal and Terylene both have ethylene glycol as monomer.





2. (1),(2),(4) Rayon consists of cellulose.
3. (1),(4) Polyester is condensation copolymer. Natural rubber is elastomer.
4. (1),(2),(3) Addition polymer can be prepared by cationic, anion in or free radical intermediate.

<H2> Linked Comprehension Type

1. (1) Elastomers have weak van der Waal force of attraction.

2. (1)

3. (4) Thermosetting polymers are hard due strong covalent bonding.

<H2> Integer Type

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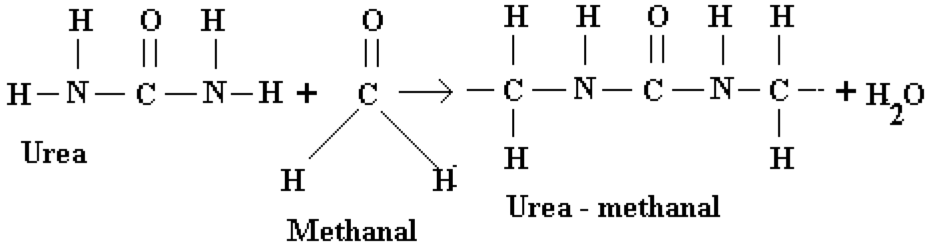
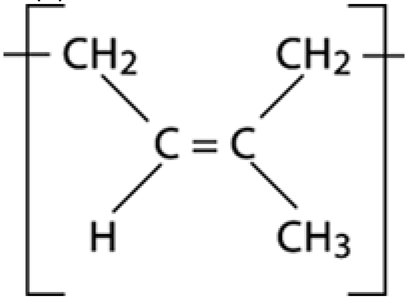
1. (2)



2. (1)



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3. (5) Natural rubber, vulcanized rubber, Buna-N, Buna-S and chloroprene.
4. (7) Polyethene, PVC, teflon, PAN.

<H2> Matrix Match Type

1. $a \rightarrow (q, r, s); b \rightarrow (q, r); c \rightarrow (p); d \rightarrow (q)$

2. $a \rightarrow (s); b \rightarrow (r); c \rightarrow (q); d \rightarrow (p)$

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